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THE ACTION OF OZONE IN THE FADING
OF ANTHRAQUINONE DYES ON
NYLON AND ACETATE

by

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The action of ozone in the fading of two selected anthraquinone disperse dyes on nylon and acetate was studied with respect to the parameters influencing the rate of fading and with respect to the type of reaction product formed with exposure.

Information was obtained by exposing nylon 6 and cellulose triacetate of varying openness of structure obtained by heat treatment or texturing, dyed with Disperse Blue 3 and Disperse Blue 7 to 20 ppm ozone in an apparatus embodying principles of AATCC Test 129-1968. The fading effects were evaluated visually or by extracting the dye and analyzing the rate of fading by spectrophotometric means. The action of swelling agents, water, benzyl alcohol, and dimethylformamide was used to study the effect on fading of nylon 6. The degradation products of ozone fading were extracted from the exposed samples, separated by thin layer chromatography, and analyzed by infrared spectroscopy using the KBr pelleton technique.

The degree of fading was found to be dependent upon accessibility of the dye in the fiber for ozone. This involves the degree of crystallinity of the fiber, the swelling state as a function of humidity or specific swelling agent, the dye penetration into the fiber, and the mode of attachment of the dye to the fiber polymer. Analysis of the rate of reaction revealed that ozone fading proceeds according to a first order law with respect to the dyestuff. This indicates equal accessibility of each dye molecule to the fading agent

provided that the fiber offers access by its swelling state.

Dyeings on nylon 6, steam textured and dry heat textured as used in this investigation, did not show a pronounced difference in rate of fading. However, the rate of ozone fading of vulnerable dyeings on nylon 66 is known to be lower when the nylon has been dry heat textured as compared to steam textured. By means of dye diffusion tests performed on the steam and dry heat textured nylon 6 used herein, it was demonstrated that there is no appreciable difference in openness of structure. The lack of differences in ozone fading rate on the nylon 6 fibers corresponded to the equivalence in openness of fiber structure.

Although Disperse Blue 7 and Disperse Blue 3 have similar ozone fading rates on secondary cellulose acetate and cellulose triacetate, the fading rate of Disperse Blue 7 on nylon 6 is much lower. A comparison was made between fading rate on nylon 6 and rate of outward diffusion of the dyes under wet bleeding conditions of AATCC Test Method 107-1968.

Moisture as a parameter in the rate of fading was found to have mainly swelling and carrier function. It does not enter the reaction chemically. On nylon 6 water can be replaced by an organic swelling agent such as benzyl alcohol and the reaction takes place with the same relative fading rates for different dyes as demonstrated with water.

The analysis of reaction products, formed with ozone exposures of Disperse Blue 3 and Disperse Blue 7 revealed a deep-seated decomposition of the dye molecules which led to loss of color rather than shade change. Under the action of ozone the anthraquinone nucleus becomes destroyed with formation of derivatives of phthalic acid.

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CHAPTER I

INTRODUCTION

The phenomenon of fading of dyed textiles on exposure to air pollutants, such as oxides of nitrogen and ozone, is known and being studied. Fading of dyes on secondary cellulose acetate caused by oxides of nitrogen has been studied since 1930. On the other hand, studies on the effect of ozone on dyed textile materials are comparatively recent.

Ozone fading, originally discovered for dyeings on secondary cellulose acetate, was found to explain fading of dyes known to be resistant to oxides of nitrogen. It also explained the fading of the same dyes on cellulose triacetate. The fading of dyes on nylon was initially considered as not to take place for either oxides of nitrogen or ozone. Therefore it was quite surprising when fadings of nylon carpets were reported which could not be traced to low light fastness since the color fading was observed in home locations with low light intensity. The two billion dollar tufted carpet industry which has come up in the last five years was confronted with this problem which turned out to be quite severe. The fading has been shown to be due to ozone or due to organic oxidants. More recently the effect of ozone has proved to be of great economic importance in the fading of permanent press fabrics despite the prior findings that dyes on polyester are free of ozone fading as most vat dyes on cotton.

Although the effect of ozone is known empirically, there has been

very little if any study of the mechanism of ozone fading of dyes. There has been no definitive study of the reasons for differences between the different fibers as to rate of fading. It is true that empirical choice of dyes and modifications of dyeing procedures have resulted in less severe fading. But there is no basis for improvement either in fibers or in dyes without a fundamental study of the mechanism of reaction by which ozone is made accessible to the fiber and the dye therein and the knowledge of the chemical changes that take place in the vulnerable dyes. The relation of fiber and dye is emphasized by the fact that Disperse Blue 7 is resistant to ozone on nylon but not on cellulose triacetate.

In order to give a logical basis to the fiber producer and to the research dye chemist as well as to the fabric finisher, a study was projected with the following objectives:

- 1) To relate the incidence of ozone fading to the factors of fiber structure affecting accessibility
- 2) To relate the structure of the dye as well as its physical state within the fiber to its rate of fading
- 3) To determine the course of the fading reaction as to its nature by study of the ultimate degradation products formed when color is lost.

The following hypotheses appeared logical and were pursued in the study:

- 1) The differences in incidence of fading and fading rate are dependent on the absorptivity and penetration of the causative

agent of ozone.

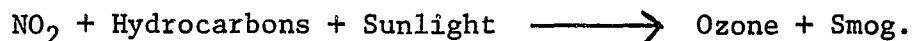
- 2) The absorptivity of the fiber for ozone will vary with the crystallinity or molecule packing of the fiber; therefore accessibility will increase when fibers are in a swollen state due to effect of absorbed water.
- 3) The resistance of dyes to ozone is dependent upon the ease of oxidation of dye structures whereby the chromophore is destroyed.
- 4) The resistance of dyes to ozone is due to the mode of attachment and the physical state of the dye within the fiber.

CHAPTER II

LITERATURE SURVEY

Occurrence of Ozone

Ozone is a normal constituent of the earth atmosphere. In a handbook of the Ozone Research & Equipment Corporation (1) it is noted that ozone is generated from oxygen by solar ultraviolet radiation of the range 1100-2200 Å. Another portion of the ultraviolet range, particularly 2200-3000 Å, causes decomposition of ozone. Due to both generation and decomposition, an ozone equilibrium is established which is subject to meteorological dynamics. Ozone concentration is dependent upon the altitude with maximum concentration occurring in the level between 12 and 20 miles up. In the lower sea level atmosphere the ozone concentration is in the order of one to five parts per hundred millions at daytime. During night time the ozone concentration is lower by reduced supply from thermal convection currents and by reaction of ozone with organic material. Ozone is also a product of atmospheric pollution. Photochemically produced smog (as in Los Angeles) contains 15 to 100 parts per 100 million of ozone. The explanation for this higher ozone concentration lies in the reaction of hydrocarbons with oxides of nitrogen which are present to a high concentration due to automobile exhausts. Schematically the hydrocarbons react according to:



Nitrogen dioxide when irradiated with ultraviolet light undergoes photochemical decomposition:



The atomic oxygen may react with oxygen in the atmosphere to form ozone directly or with hydrocarbons to form aldehydes and peroxides.

According to Haagen-Smit (2) these peroxides can form ozone:



Occurrence of Ozone Fading of Dyes

The general principles involved in the fading of dyes by atmospheric pollutants were presented by Salvin (3) as:

- (1) The dye should be sensitive to the chemical agent causing dye destruction
- (2) The chemical agent should be present in sufficient concentration to cause destructive action
- (3) The chemical agent should be absorbed by the substratum in which the dye is present
- (4) The test procedures should be adapted to the specific fiber and should correlate with actual service exposure

Secondary Cellulose Acetate and Cellulose Triacetate

The phenomenon of gas fading (fading caused by oxides of nitrogen) has long been recognized and was initially described by Rowe and Chamberlain (4) in 1937. Blue shades and shades where blue dye is present as a component on secondary cellulose acetate were shown to exhibit reddening on exposure. Rowe and Chamberlain pointed out that the decomposition that occurs in fading may be due to diazotization,

nitrosation, or oxidation of the dyestuff. Couper (5) has shown the oxidative nature of oxides of nitrogen on 1,4-Di (methylamino) anthraquinone by identification of a number of degradation products. Salvin (6) in his search for disperse dye structures which are resistant to gas fading, synthesized blue disperse dyes which exhibit high resistance to oxides of nitrogen in AATCC Test Method (AATCC = American Association of Textile Chemists and Colorists). In an actual exposure test, acetate drapery fabrics dyed with these gas resistant dyes were placed in Pittsburgh, Pennsylvania, and in Ames, Iowa. Reddening of the AATCC test ribbon for oxides of nitrogen indicated high nitrogen oxides concentration in Pittsburgh, the absence of reddening a low concentration in Ames. At the end of the exposure period, the gas fading resistant dyes were found to be unchanged in Pittsburgh but changed in Ames. Salvin and Walker (7) showed evidence that ozone could be responsible for the change. With exposure to ozone concentration of 10 parts per 100 million generated by ozone lamps, these workers could duplicate the service test. They found that all blue anthraquinone disperse dyes were sensitive to ozone as well as certain red anthraquinone dyes.

The lack of fading in Pittsburgh was explained by the high sulfur dioxide content in the atmosphere, caused by coal burning. The ozone becomes consumed in oxidizing sulfur dioxide to sulfur trioxide which made the Pittsburgh atmosphere low in ozone. In Ames, normal quantities of ozone were sufficient to cause dye failure on acetate. Salvin (3) also mentioned ozone fading of disperse dyes on cellulose triacetate. The fading rate of cellulose triacetate dyeings was shown

to be slower when they were heat treated at 400° F for 30 seconds.

A marked decrease in fading rate was observed with the formation of a surface layer of cellulose by ring saponification. No definitive explanation is offered.

Nylon

Disperse Dyeings on nylon were also found to be subject to ozone fading. Salvin (3, 8) reported about complaints concerning fading of nylon carpets, both nylon 66 and nylon 6, where primarily loss of blue was observed. Analysis revealed that Disperse Blue 3 was the dye used. Low lightfastness could not have been the cause for the fading since the color changes were observed in home locations with a low light intensity. Standard tests for oxides of nitrogen, ozone and sulfur dioxide which were made with the same material did not duplicate outdoor exposure tests in Florida. Most of the fading complaints came from coastal areas of Texas and Florida which labeled this type of fading "Gulf Coast Fading". The hot, humid climate of these areas led to the conclusion that humidity was a factor in fading of these nylon carpets. Ozone fading tests run under high humidity (80-90%) showed pronounced changes of disperse blue dyestuffs on nylon carpets which were equal to the change observed in actual outdoor exposures.

In order to provide a test procedure for this kind of fading, the AATCC (9) developed in addition to their Test Method 109-1963, Colorfastness to Ozone in the Atmosphere, the Test Method 129-1968, Colorfastness to Ozone in the Atmosphere Under High Humidities. In both tests a test specimen and a swatch of control sample are simultaneously

exposed to an atmosphere containing ozone until the control sample shows a color change corresponding to that of a standard of fading. The conditions for the high humidity test are set on 85-90% relative humidity and $104 \pm 9^{\circ}$ F ($40 \pm 5^{\circ}$ C). The control sample for Test Method 109-1963 consists of a medium shade of grey cellulose triacetate which is ring dyed using Disperse Blue 27 as one component. This dye is fast to oxides of nitrogen but not to ozone. The control sample for Test 129-1968 is a tertiary shade, avocado, prepared by dyeing nylon 6 with a combination containing Disperse Blue 3, Disperse Yellow 3, and Disperse Red 55.

Permanent Press

Polyester/cotton fabrics as originally dyed with disperse dyes and vat dyes respectively are not vulnerable to atmospheric contaminants. Salvin (3, 10, 11) reported about fading of polyester/cotton permanent press fabrics which have been subjected to postcuring or precuring. This fading was observed on the shelves of retail stores or in the warehouses of the cutters. Ozone was found to be the major cause for the color changes observed, and some change was contributed by oxides of nitrogen. According to Salvin it is the fading of the Disperse dye which had migrated from the polyester to the finish during the precuring or postcuring operation. The dye migrated mainly to non-ionic surfactants and softeners which were present in the finish. Softeners represent a completely different medium for the dye in which ozone fading occurs. This phenomenon is at the same time a proof for the importance of the nature of the substratum containing the dye.

Actually one cannot speak about the fastness in general and about ozone fastness in particular, but only about the fastness of dye--substratum system.

Accessibility and Fiber Structure

Fibers consist of unbranched polymer molecules which have repeating features. These polymer chains are arranged more or less ordered parallel to the longitudinal axis of the fiber. Due to the regularity of the structure the polymer chains can be in a state of three dimensional order, the crystalline state. When the chainlike molecules of the solid fiber polymer are in a state of disordered arrangement they are said to be in an amorphous state. Peters (13) discussed the fine structure of fibers and the dependence of fiber properties on the degree of crystallinity and orientation. He stated that accessibility of the fiber system is dependent upon the existence of the rather open amorphous regions, like moisture sorption and dyeing. Increase in orientation decreases the ease which dye molecules or chemical reagents can penetrate.

Stoll (14) explained the difference in crystallinity between secondary cellulose acetate and cellulose triacetate with the different substitution pattern. In cellulose triacetate all three hydroxyl groups per glucose unit of the cellulose are replaced by acetyl groups, whereas in secondary cellulose acetate only about two and one-half of the three OH groups per glucose unit have been replaced. This makes triacetate cellulose more regular and this makes it possible for the chain molecules to associate with each other in a more perfect order. In

secondary acetate the acetyl and hydroxyl groups are irregularly distributed along the molecular chain; its tendency for crystallization is much lower. It follows that secondary acetate is more accessible to penetration of dyes and chemical reactants. Stoll showed in a graph the much lower dyeing rate for cellulose triacetate compared to secondary cellulose acetate. The dyeing rate is raised considerably for cellulose triacetate by use of dyeing accelerants. The function of tripropyl phosphate as accelerant in dyeing cellulose triacetate is according to Fortess (15)

- (1) Solubilization of crystalline dyes in the aqueous phase
- (2) Absorption onto the fiber surface providing a dye solvent at the fiber-liquor surface
- (3) Absorption into the fiber, swelling the fiber and weakening molecular bonds, permitting easier access for dye diffusion into the fiber.

Stoll (14) pointed out that wash fastness of cellulose triacetate dyeings are higher than those on secondary cellulose acetate when cellulose triacetate is submitted to a heat treatment after dyeing. This heat treatment causes uniform dye distribution throughout the fiber and modifies at the same time the crystalline structure of the fiber which causes lower dye diffusion rates. The reason for the higher degree of crystallinity after heat treatment was explained by the thermal agitation which allows a rearrangement of molecules in amorphous regions whereby larger crystals are formed. The degree of crystallinity and the average crystallite size increases above a certain critical temperature region. Jellinek (16) found that this critical temperature region is dependent upon the applied stress during heating.

He also discussed the connection between the degree of order in cellulose triacetate and its dyeing properties.

Similar to other textile fibers, the internal structure of nylon can be characterized by its amorphous portion, crystalline portion and a portion of intermediate order. In the texturing process heat is applied to impart the desired crimp into this thermoplastic fiber. With such a process structural changes take place which are dependent upon the conditions by which the heat is transferred. Peters and White (7) observed that the dyeing rate for dry heat textured yarn is lower than for steam textured yarn. It follows that steam textured yarn has a more open structure and therefore is more accessible. Rau and Schwair (18) investigated the structural changes of nylon 6 with dry heat and steam fixation using infrared spectroscopical methods. With the dry heat treatment, they found an increase in crystalline order and a decrease in amorphous and intermediate order. With saturated steam an increase of the crystalline part as well as of the amorphous part on the expense of the portion of intermediate order was observed. Steam acts as a swelling agent which is able to penetrate the intermediate order portions. By pushing apart the molecular chains steam causes an increase of amorphous regions and renders steam textured nylon more accessible to dye and to other agents.

Reactivity of Dyes

The evaluation of ozone fading of dyes as related to their structure was originally reported for a wide-spread range of dyes by

Salvin and Walker (19). For blue amino anthraquinone dyes these workers found a relation between resistance to ozone fading and nucleophilicity of the alkyl- or arylamino nitrogen in the amino anthraquinone dye. A reduction in nucleophilicity of this vulnerable nitrogen will also reduce the reaction with the strongly electrophilic ozone. By synthesizing a series of arylamino analogs of some basic amino anthraquinone dye structures and checking the colorfastness of dyeings made with them this relation was shown. Salvin and Walker (20) noted that diphenylamine dyes which are yellow are completely resistant to air contaminants. In the azo range of dyes the degree of change of the reds is less than that of the blues. Thus, Setacyl Blue G, an azo blue, is vulnerable to the effect of ozone whereas azo red dyestuffs, represented by Disperse Red 35, are resistant. Anthraquinone red dyestuffs generally of 1-amino-4-hydroxyanthraquinone structure will change on ozone exposure. This is shown by testing procedures and by service tests on cellulose triacetate yarns and on nylon carpets (Celanese Technical Information Bulletin 15). In the case of anthraquinone blues on cellulose triacetate all disperse blue dyestuffs are sensitive to ozone fading. This sensitivity bears no relation to lightfastness or to resistance to oxides of nitrogen fading. There are some differences among blue anthraquinone dyes with respect to ozone fading but these differences are of degree rather than of kind. Salvin (21) found that upon exposure of equivalent blue shades on cellulose triacetate in ozone environments either in laboratory or in service, a change is noted within three to six months. This change is sufficient to characterize all anthraquinone disperse

blues on cellulose triacetate vulnerable to ozone.

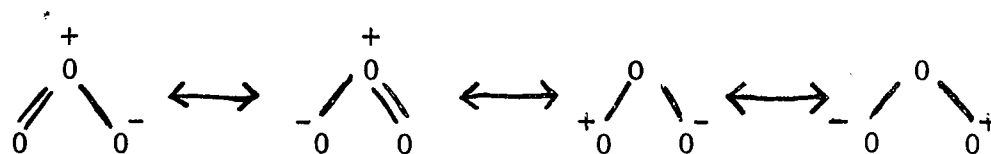
In case of nylon, however, a variation in resistance to ozone fading of anthraquinone blue dyestuffs is recognized (3). This difference is used in the recommendation for dyeing nylon carpets for commercial resistance to ozone fading (Beaunit Bulletin). Thus, Disperse Blue 3 shows catastrophic fading in periods within 90 days, whereas Disperse Blue 7, also an anthraquinone dye, shows only mild change which gives retention of shade. This difference in degree of change in nylon versus that of cellulose triacetate suggests that the mode of attachment of dye to the fiber might be a fruitful hypothesis to explore.

It should also be noted that a series of acid dyes of anthraquinone structure are used for dyeing nylon carpets. According to Taylor (22) these dyes exhibit excellent resistance to ozone fading, for example Acid Blue 25. This high resistance of acid dyes further suggests that the mode of attachment of the dye molecule to the fiber might be used to explain resistance to ozone fading.

Reaction of Ozone with Aromatic Ring Compounds

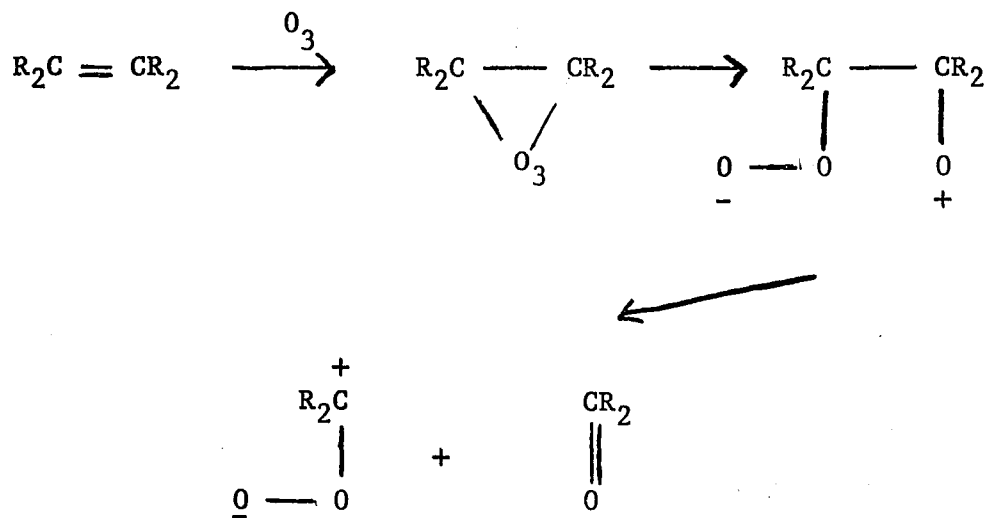
A survey of the literature does not show any previous work which deals directly with the action of ozone on anthraquinone dye structures from the standpoint of site of attack and degradation products.

Ozone is a highly reactive compound of electrophilic nature, and may be represented as a resonance hybrid of four structures:

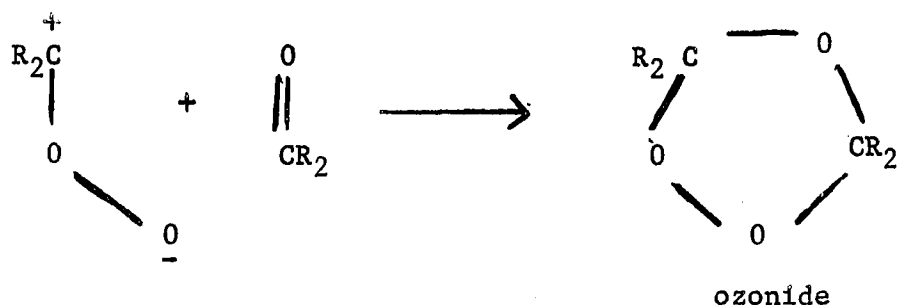


Ozone is an excellent reagent for double bonds in organic compounds. In this function, it is used as an analytical reagent for determining the location of double bonds.

Reacting with double bonds ozone breaks both carbon-carbon bonds with the formation of cyclic peroxides known as ozonides. The mechanism of this reaction has been investigated largely by Criegee (23, 24). The first step is the addition of ozone to the olefin to give an "initial ozonide". This species is unstable and forms a zwitterion which in turn breaks apart to form an aldehyde or ketone and a different zwitterion:



These products combine again to form an ozonide:



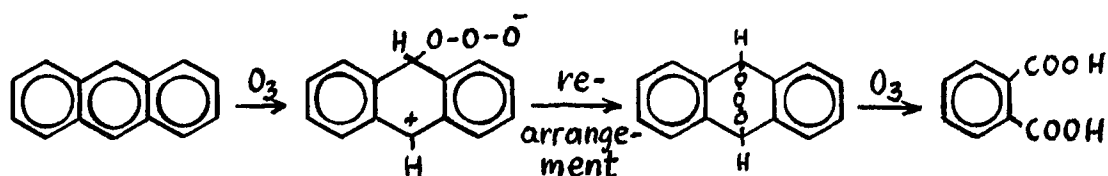
The ozonide can be decomposed by reduction to give aldehydes or ketones. According to Sousa and Bluhm (25) ozonides can also be oxidized with oxygen or hydrogen peroxide to give ketones and/or carboxylic acids.

Olefins as well as aromatic compounds are attacked by ozone. Aromatic compounds are less readily attacked than olefins. Mosher (26) stated that the addition of ozone to aromatic double bonds proceeds at about 10% the rate of isolated double bonds. According to March (27) the aromatic ring compounds behave toward ozone as if the double bonds in the Kekulé structures were really there. He noted that benzene forms three moles of glyoxal with ozonolysis. With polycyclic aromatic compounds, however, the site of attack is dependent upon the structure of the molecule. Ozonolysis reactions are also governed by the solvent in which the reaction takes place.

Bailey et al. (28) studied quite extensively the reactions in the ozonization of anthracene. With the reactions anthraquinone is formed as well as phthalic acid. The ratio of the reaction product is dependent upon temperature and solvent used. There is also a dependence upon the ozone concentration. Ten millimoles anthracene with 3.0-3.6 mole-equivalents of ozone in carbontetrachloride at -20°C yields

65% pure phthalic acid (Bailey). The fact that phthalic acid is formed is evidence for the potential of ozone to cleave polycyclic ring systems. According to Bailey et al. the formation of phthalic acid with the ozonization of anthracene arises mainly from an initial attack on the central ring.

Schematically:

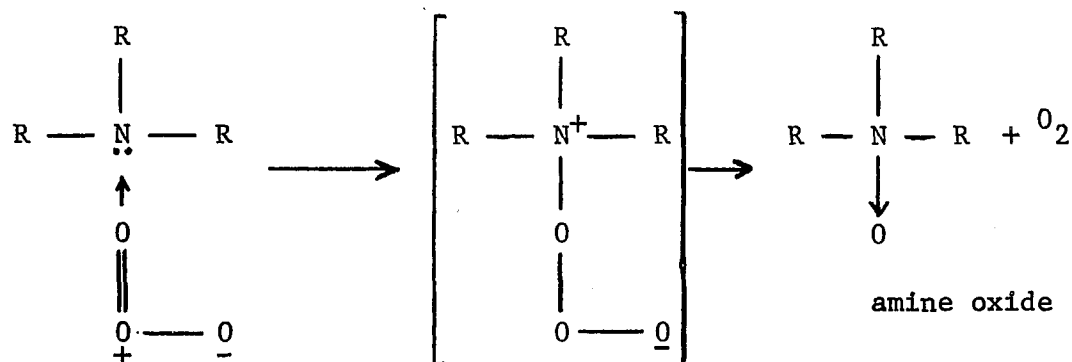


Anthracene

Phthalic acid

These workers, however, reported also a minor competing bond attack on an outer ring, which also produced phthalic acid.

Ozone as a strong electrophilic reagent can attack nucleophilic centers, for example the nucleophilic nitrogen in amines. Maggiolo and Niegowski (29) reported about the action of ozone on tertiary amines. The reaction is explained as an electrophilic attack of the terminal oxygen of ozone on the nucleophilic nitrogen.



CHAPTER III

PROCEDURES

Design of Experiments

The following experiments were planned to show the relationship between fiber structure and incidence of fading. They were designed to distinguish between the fading potential of surface dye (ring dyeing) and the fading of well penetrated dye as affected by accessibility and variation in openness of fiber structure. Such a variation in dye accessibility to the ozone reactant was obtained in case of cellulose triacetate by:

- a) Dyeing at 85°C without dyeing accelerant, which is known to give ring dyeing (Technical Bulletin TBT4, Celanese Corporation). In fact the ozone control ribbon used in AATCC-Test 109-1963 is such a ring dyeing.
- b) A fully penetrated dye was obtained by the use of a dyeing accelerant. Trichlorobenzene (Tanavol NB) was used because it is known to have no permanent effect on the physical nature of the fiber although its effect is to swell. The dyeing temperature was 95°C which is required for good penetration. The procedure involves a good scouring after dyeing and a low temperature drying to volatilize any residual trichlorobenzene initially absorbed by the fiber. Residual dyeing accelerant can be expected to increase the rate of fading due to its

swelling characteristic.

- c) Heat treatment (one minute at 200°C) of a dyeing made without accelerant. This heat treatment serves a double purpose: full penetration of dye and internal change of physical structure toward lower accessibility.
- d) Heat treatment of a dyeing made with accelerant. Here again the physical properties of the fiber have changed; a greater packing of the molecular chains is obtained.

In order to demonstrate the effect of swelling on the accessibility to ozone these dyeings were exposed to ozone both under dry and under moist conditions.

In addition to cellulose triacetate, secondary cellulose acetate was used in exposure experiments. This fiber has a more open structure, higher hydrophilicity, shows a good penetration of dye without accelerants and is prone to ozone fading.

The dyeings for the just described study were made in one depth using Disperse Blue 7. In all the other experiments which will be described Disperse Blue 7 as well as Disperse Blue 3 was used in order to compare the fading behavior of two different dye structures. Disperse Blue 7 is considered faster to ozone fading on nylon than Disperse Blue 3 but equivalent on cellulose triacetate. The difference in their fastness could be due to the mode of attachments and the physical state within the fiber. In comparing the rate of fading of these two dyes, the influence of dye structure and accessibility on fading reactions can be studied.

Disperse Blue 3 has not been used for the study involving heat treatment of cellulose triacetate because of its sublimation tendency. Disperse Blue 3 sublimates under the conditions of the heat treatment necessary for structural changes in cellulose triacetate.

Disperse Blue 3 and Disperse Blue 7 are used commercially to a great extent and contain 33-35% actual dye with the remainder consisting of surfactants. Both dyes are not uniform but are rather complex mixtures of dye structures. These commercial dyes rather than purified ones, were used in order to make the study relevant to the actual behavior already reported for fading. The dyeing procedures carried out were also in approximation to procedures used in practice.

The cellulose triacetate and secondary cellulose acetate fabrics used in this study were supplied by Celanese and are characterized in the section "Materials". Their identity was checked by acetone solubilities.

Informations about accessibility of the particular dye to the reactant can be obtained from rate studies. Therefore the fading rates for both dyes on cellulose triacetate and secondary cellulose acetate were determined and compared. The dyed fabrics were exposed to ozone under low humidity conditions according to AATCC 109-1963 for 12, 24, 36, and 48 hours. The data for the rate of fading were obtained by analyzing methanol extracts of the exposed samples. Methanol was used because it represents a good solvent for the dye and is very suitable for transmission measurements due to its very low light absorption.

The ozone fading of nylon carpets bears a great economic importance.

In order to check the hypotheses stated at the beginning as to their validity, textured nylon 6 in carpet denier was used for experimentation. The material supplied by Allied Chemical Corporation was obtained in dry heat textured form as well as in steam textured form. The differences in openness of structure were checked indirectly by dyeing trials and by outward diffusion trials with wet bleeding tests using AATCC Test Method 107-1968.

The dyeings were carried out with Disperse Blue 3 and Disperse Blue 7, using commercial dyes as with cellulose triacetate, under conditions approximated to commercial practice. In the ozone exposure the humidity was controlled using the ozone fading control (avocado shade on nylon 6 carpet) according to AATCC Test Method 129-1968. These experiments served to show the effect of humidity as related to openness of structure.

The rate of fading for Disperse Blue 3 and Disperse Blue 7 on dry heat textured and steam textured nylon was determined for three different concentrations. This was done in order to see whether the fading rate and fading reaction is influenced by the concentration of dye in the fiber. Usually with higher concentrations the dye tends to aggregate within the fiber which would influence its accessibility to ozone.

The data for the rate of fading were again obtained by analyzing methanol extracts of the exposed samples.

In order to compare ozone fading for Disperse Blue 3 and Disperse Blue 7 on the same and on different substrata it would be advantageous

to express the dye concentrations as molar concentrations. To arrive at an approximation the average molecular weight of the dyes were determined by finding the proportions in which the main components are present in the dye and from infrared spectra by which the components were related with the structure.

The function of humidity in ozone fading was also studied in connection with the following questions:

- 1) Is water within the fiber necessary as carrier for the fading reactant and as the reaction medium?
- 2) Does water enter into the reaction chemically, in other words, is the presence of water specifically necessary for the ozone fading reaction?

In order to attack these questions two different lines of experiments were performed:

- a) Dyed secondary cellulose acetate was exposed to ozone with low humidity or without humidity
- b) Dyed nylon was exposed to ozone under low humidity or without humidity but impregnated with organic solvents or swelling agents.

The experimentation was only qualitative in nature, and no quantitative data were collected.

The overall picture of the reaction of ozone with dyestuffs is that of an oxidation reaction. In order to learn whether the same fading criteria are valid with respect to accessibility with the exposure to oxidants other than ozone a series of experiments was

performed. Cellulose triacetate, secondary cellulose acetate, nylon dry heat textured, and nylon steam textured, all dyed with Disperse Blue 3 as well as with Disperse Blue 7, were exposed to sodium hypochlorite solution and to hydrogen peroxide solutions.

Although NO_2 is not considered as being a significant fading agent for nylon carpets, it was of interest to know whether the dye in nylon is also accessible to NO_2 under moist exposure conditions. Experiments in this direction were performed.

In order to learn about the course of the fading reaction as to its nature, degradation products formed with ozone exposure of the dyes used were isolated and some of them analyzed. Many degradation products are only present in minute quantities after the reaction is stopped, which made their analysis difficult or even impossible with the experimental facilities available for this study.

Before degradation products can be studied the undegraded components of the dyes have to be known. Thin layer chromatograms were made of the dyes used and the R_f values determined in order to recognize undegraded dye out of more complicated chromatograms made from exposed dye.

The course of fading was followed by making chromatograms with the dyes extracted from the exposed samples for the rate study. Some intermediates of the reaction appear to be very short living. In order to identify one of the intermediates of the reaction of Disperse Blue 3 with ozone, the dye was exposed on a thin layer plate. The silica gel coating of the thin layer plate represents a different

absorbent for the dye which exhibits also different accessibility characteristics compared with the textile material. Therefore the rates of fading of dyes and intermediates can be expected to be different on silica gel.

Degradation products from exposures on the different textile substrata were extracted, separated, and isolated by thin layer chromatography technique and analyzed using their infrared spectra.

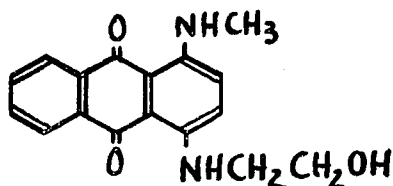
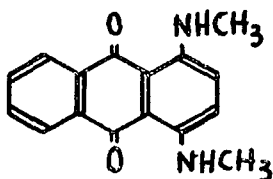
Experimental

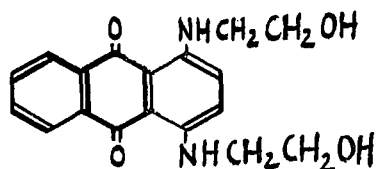
Materials

Dyes Used

The following commercial dyestuffs were used:

- 1) Celliton Fast Blue FFRN extra concentration (GAF) Color Index Disperse Blue 3, 61505. This dye is not a uniform compound but mainly a mixture of the following three 1,4-alkylamino anthraquinones:



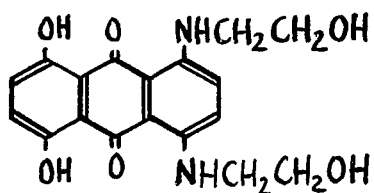


The dye is made by condensation of quinizarin with a number of aliphatic amines, i.e. methylamine, hydroxy ethylamine. Ammonia is sometimes added for shading purposes. Chromatographic examination of this dye revealed six different compounds. The quantity of the three compounds other than the above indicated ones is very small; they appear to be 1-alkylamino-4-hydroxy anthraquinones.

2) Artisil Blue Green G (Sandoz)

Color Index Disperse Blue 7 62500

This dye is also not uniform. The chromatogram shows 7 components, two of them in high concentration. The other five components are impurity range. The major component, a greenish blue, has the structure:



The other component comprising 30% of the major component is a neutral blue. Its infrared spectrum exhibits the same groupings as the major component. The difference in shade is thought to be due to variability in oxidation forms. The manufacture of Disperse Blue 7 requires a special oxidation process to attain the desired shade and dyeing properties.

The dye is made by condensation of leuco 1, 4, 5, 8-tetrahydroxy anthraquinone with hydroxyethylamine.

Substrata Used

- 1) Secondary cellulose acetate fabric (Celanese) made with a 75/RSMZ/20 bright warp and a 150/2Z/40 bright filling in plain weave.
- 2) Cellulose triacetate fabric (Celanese) made with a 100/2Z/26 dull warp and a 150/2Z/40 dull filling in plain weave.
- 3) Sleeves of nylon 6 (Allied Chemicals)
 - a) dry heat textured
 - b) steam textured

made with a yarn of 1175 denier containing 70 filaments.

Ozone Fading Equipment Used

The ozone fading equipment used is one adapted for higher humidity ozone exposure. In principle it is based upon the concept of generation of ozone outside the exposure chamber since the passage of air containing high humidity over the ozone generator gives reduced formation of ozone. General Electric Ozone lamps are used. High humidity is obtained by heating water which is placed on the bottom of the chamber. The principle in design of the test chamber is shown in Figure 1 which has been copied from an article by Salvin (3).

Figure 1

Principle of High Humidity Ozone Chamber

A commercial adaption of this design was made by South Eastern Aniline Corporation, whose apparatus is shown in Figure 2.

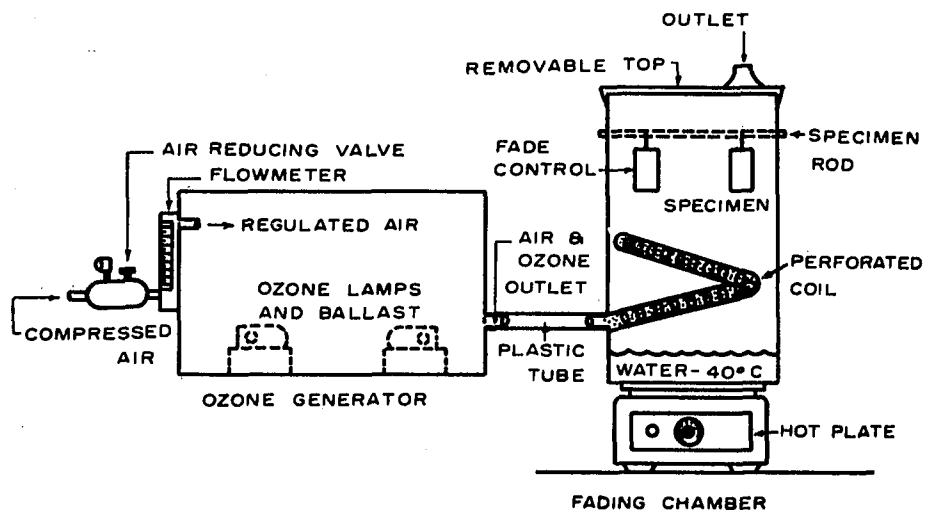
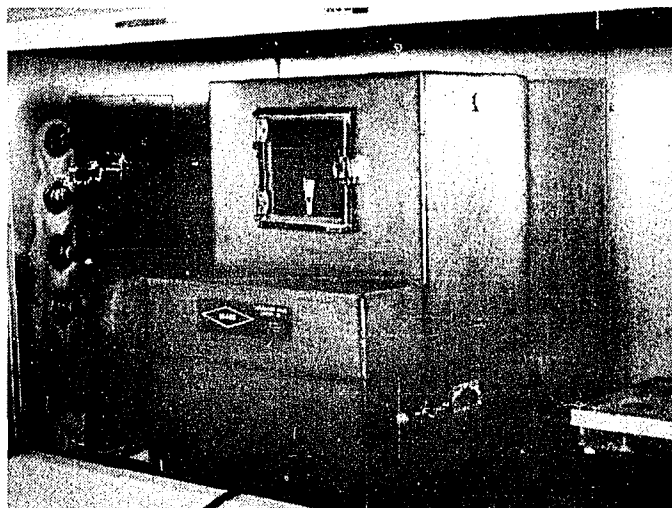


Figure 2

South Eastern Aniline High Humidity Ozone Chamber



As a modification forced draft is used rather than compressed air. This testing equipment has been approved for use in AATCC Test Method 129-1968.

The ozone concentration provided by this chamber was measured with an ozone meter model 724-2 manufactured by Mast Development Company. The ozone concentration within the chamber was found to be 18 to 20 parts per hundred million per volume. The chamber works in a reproducible manner which was checked by a series of runs under the same conditions using AATCC fading control samples as substratum.

Instrumentation

The Beckmann DK-2A ratio Recording Spectrophotometer was used for transmission measurements over the visible spectrum. A matched pair of stoppered quartz cells, each 10mm in length, were used for sample and reference solution. Methanol was used as solvent for both the sample and the reference.

For infrared absorption measurements two instruments were used: the Beckmann-IR5A Infrared Spectrophotometer and the Perkin-Elmer Model 457 Grating Infrared Spectrophotometer. The samples were examined using the potassium bromide pelleton technique. For this the compounds to be analyzed were intimately mixed with approximately 100mg dry potassium bromide which was effected with a vibrating ball mill. With these KBr-sample mixtures transparent discs were obtained by pressing using a simple bolt and nut device.

Methods

Preparation

Samples to be dyed were scoured using 0.5 gram per liter Triton X-100 (Rohm & Haas) for one half hour at 75°C.

Dyeing

Except for the dyeing of cellulose triacetate with dyeing accelerant the procedure used was the same for all materials: 25g samples were dyed in three different concentrations of dye, 0.25%, 0.5%, and 2% of sample weight. The dyeings were performed at a liquor ratio of 1:30 at 85°F for 90 minutes at pH 8. The dye liquor was brought on temperature before entering the material to be dyed. After dyeing the samples were thoroughly rinsed and left neutral. The dyed samples were kept in the dark and sealed.

For the dyeing of cellulose triacetate with 0.5% Disperse Blue 7, using an accelerant, 5% of fabric weight Tanavol NB (Tanatex Chemical Corporation) was added to the dyeing bath. Liquor ratio was 1:30, the dyeing temperature 95°C. Dyeing time 90 minutes. After dyeing the sample was thoroughly rinsed and scoured with 1 gram per liter Triton X-100 for 30 minutes at 75°C.

Heat Treatment

Two 10gram samples of cellulose triacetate dyed with 0.5% Disperse Blue 7 were given a heat treatment in an oven (Precision Scientific Co.) at 200°C for two minutes. The procedure was to raise the oven temperature to 200°C at which time the fabric was placed in the oven.

Two minutes were used in order to provide enough time for the fabrics to heat up and to compensate for the cooling off caused by opening the door.

Ozone Exposure

The exposures were performed according to AATCC Test Method 109-1963 for dry conditions and AATCC Test Method 129-1968 for moist conditions. In order to get the minimum of 80% relative humidity for the moist exposures a higher temperature as required in the AATCC Test Method had to be used. A chamber temperature of 50°C was necessary. Exposure times were varied in order to perform rate studies. The exposure time was also checked with AATCC fading control samples for the specific method.

Extraction

The exposed and unexposed samples were extracted on a set of soxhlets. Methanol was used as a solvent for all substrata and for both dyes. No problems were encountered with extracting secondary cellulose acetate and cellulose triacetate. Disperse Blue 3 on nylon was also easy to extract except for one degradation product which did not come off and which is thought to have formed an ionic bond with nylon. The extracted exposed Disperse Blue 3 nylon samples exhibited therefore a brownish color. Disperse Blue 7 on nylon was not completely extractable with methanol. A blue tint remained on the fiber. Since this remaining dye concentration on the fiber was so minute, it was considered negligible and the methanol extraction procedure was used.

Dye Determination

The dye concentrations of the extracts were determined by spectrophotometric means. The relation between amount of light absorbed and the concentration of a dye in solution is given by Beer's law. Since cells of 1cm (10mm) thickness were used in all measurements and the solvent as reference, Beer's law was used in the following simple form:

$$A_s = k \cdot c$$

A_s = absorbance of the solution, defined by

$$A_s = \log_{10} \frac{1}{T_s}$$

T_s = transmittance

k = constant, dependant upon the wavelength

c = concentration

Beer's law was found to be obeyed for the dye concentrations used. In order to determine the k values for the dyes used at the selected wavelength standard solutions of these dyes with known concentrations were prepared and k values were obtained according to

$$k = \frac{A_s}{c}$$

With these k values and determined absorbance data of the solutions the dye concentrations were determined. The dye used for preparing the standard solutions was extracted with acetone from the commercial sample in order to remove the dispersion agent and other additives and to arrive at k values for the actual dye content of the colorant.

The absorbances of the dyes were measured at room temperature.

Separation

Thin-layer chromatography technique was used for separating the components of the unexposed and exposed dyes. The principle of this technique is to accomplish separation by successive equilibrations of the sample components between two phases, one of which moves over the other. With the used adsorption chromatography technique the stationary phase constitutes a thin layer of adsorbent which is supported and held in place by a glass plate. The sample is placed on this adsorbent. The mobil phase which moves descending or ascending by capillary action through the thin layer causes the separation. The more polar the solvent the greater the migration which is produced. However, a solvent which elutes the solutes too fast will not separate them. It is quite a tedious work to find the right solvent combination for the particular system under investigation, since adsorption properties of layers vary widely. The degree of retention for the particular solute is expressed as the retardation factor, R_f :

$$R_f = \frac{\text{distance solute moved}}{\text{distance solvent moved}}$$

In this work Adsorbosil-5, made by Applied Science Laboratories, Inc., State College, Pennsylvania, was used as adsorbent. It is a purified silica gel without any binder or fluorescent pigment. The layers were applied on glass plates using a spreading device manufactured by Desaga, in Germany. This apparatus is characterized by a moving reservoir, where the aquaous slurry of the adsorbent powder is put in, and stationary plates. The reservoir is passed over the plates

producing the desired layer thickness. The normal layer thickness is 0.25mm. For this work a thickness of 1mm was chosen in order to get a higher capacity out of the plates and larger amounts of separated compounds for further work up. After coating the plates were air-dried overnight. Before using the layers were activated by heating them at 100°C for half an hour.

The compounds to be separated were applied to the plates by a streaking device. With this device a fine jet of sample solution is blown from a syringe into the layer while moving the syringe in a uniform motion over the plate. The result is a thin uniform streak with known concentration of solute. For development of the "streaked" plates a tank was used in which the solvent system was placed on the bottom. After inserting the plates the tank was covered by a glass plate. The walls of the tank were not covered with solvent impregnated filter paper since for the kind of separation performed a vapor pressure equilibrium within the chamber turned out to be not necessary. For the development of Disperse Blue 3 the following solvent combination were found to be suitable:

n - hexane 7 parts

acetone 3 parts

For Disperse Blue 7 the solvent mixture used was:

benzene 4 parts

acetone 1 part

In most cases the separated compounds were visible either by their color or by their fluorescence under ultraviolet light. For detecting

uncolored and non-fluorescent compounds, test chromatograms were sprayed with sulfuric acid and heated. This causes organic compounds to carbonize which can be seen by the black color. For further analysis the separated bands on the thin layer plates were scratched off with a spatulum and placed separately in small beakers. In order to separate the silica gel from the compound, solvent was poured successively into the beakers, the solution decanted into tubes. The tubes were placed into a centrifuge and spun at 3000 revolutions per minute for five minutes. With this procedure the silica gel sedimented on the bottom of the tube. The solution on top was pipetted off and placed in another tube. Another cycle of centrifugation was necessary to get the solutions free from silica gel. Finally the solutions were placed in beaker and the solvent evaporized in the oven at moderate temperatures (40°C). The compounds thus separated were used for further analysis.

Identification of Fading Products

The separated fading products were analyzed by infrared spectrophotometry.

Infrared absorption promotes molecular vibrational changes. Since atoms have different masses and bond strength (length) varies, different combination of atoms will vibrate at various frequencies when the molecule absorbs electromagnetic energy of appropriate frequency. Only those vibrations that result in a rhythmical change in the dipole moment of the molecule can be observed by infrared spectroscopy. The alternating electric field, produced by the changing charge

distribution accompanying a vibration, couples the molecular vibration with the oscillating electric field of the electromagnetic radiation. One can distinguish between stretching and bending vibration since they give rise to absorption at different wavelength. Thus even simple molecules can give an extremely complex spectrum. Since it is unlikely that any two different compounds give the same infrared spectrum a peak-by-peak correlation of an unknown compound against that of an authentic sample is excellent evidence for identity. Although the infrared spectrum is characteristic of the entire molecule, certain groups of atoms give rise to bands at or near the same frequency regardless of the structure of the molecule. Thus, useful information can be obtained by inspection for characteristic group frequencies.

Group frequency inspection of infrared spectra obtained from fading products and also correlation with spectra from infrared spectra collection of known compounds (30) were used in this work.

Exposures

Study of the Effect of Dye Penetration and Fiber Structure

2.5 gram swatches of the following dyeings were exposed to dry as well as to moist ozone:

- a) Cellulose triacetate dyed with 0.5% Disperse Blue 7
- b) Cellulose triacetate dyed with 0.5% Disperse Blue 7, heat treated after dyeing
- c) Cellulose triacetate dyed with 0.5% Disperse Blue 7, using a dyeing accelerant
- d) Cellulose triacetate dyed with 0.5% Disperse Blue 7, using a

dyeing accelerant and heat treatment after dyeing

Dry ozone exposure conditions:

relative humidity 25%; temperature 22°C

exposure time 12 hours

Moist ozone exposure conditions:

relative humidity 80%; temperature 45°C

exposure time 12 hours

Rate Study

Secondary cellulose acetate and cellulose triacetate:

Four 5 gram swatches of each of the following dyeings were placed in the ozonizer and exposed according to AATCC Test Method 109-1963 (dry conditions) together with a piece of ozone control fabric.

- a) Secondary cellulose acetate, 0.5% Disperse Blue 3
- b) Secondary cellulose acetate, 0.5% Disperse Blue 7
- c) Cellulose triacetate, 0.5% Disperse Blue 3
- d) Cellulose triacetate, 0.5% Disperse Blue 7

Each 12 hours a sample set was removed to obtain 12, 24, 36, and 48 hours exposed samples for each of the two dyes used on the two substrata.

Nylon 6, dry heat textured and steam textured:

Four 2.5 gram swatches of each of the following dyeings were placed in the ozonizer and exposed to AATCC Test Method 129-1968 (moist conditions) together with a swatch of the avocado carpet control.

Dry heat textured nylon dyed with

- a) 0.25% Disperse Blue 3
- d) 0.25% Disperse Blue 7

- b) 0.5% Disperse Blue 3 e) 0.5% Disperse Blue 7
- c) 2.0% Disperse Blue 3 f) 2.0% Disperse Blue 7

Steam textured nylon dyed with:

- a) 0.25% Disperse Blue 3 d) 0.25% Disperse Blue 7
- b) 0.5% Disperse Blue 3 e) 0.5% Disperse Blue 7
- c) 2.0% Disperse Blue 3 f) 2.0% Disperse Blue 7

Each 12 hours a sample set was removed to obtain 12, 24, 36, and 48 hours exposed swatches for each of the combination listed.

Study of the Function of Humidity

Exposures of dyed nylon to ozone were performed under low or without humidity, but impregnated with organic solvents or swelling agents. For each of the following experiments four samples were prepared:

- a) control
- b) immersed in organic solvent, air dried
- c) immersed in organic solvent, exposed to dry ozone
- d) exposed to dry ozone

Table 1
Exposure Experiments for Dyed Nylon to Ozone under
low Humidity with Organic Solvent

Nylon substratum	Humidity	Temperature	Organic solvent	Exposure time equivalent to cycles
steam textured dyed with Blue 3	4%	40° C	Dimethyl formamide	2
ozone control sample (avocado)	4%	40° C	Dimethyl formamide	2
ozone control sample (avocado)	4%	40° C	Benzene	1
ozone control sample (avocado)	3%	40° C	Benzyl alcohol	2
ozone control sample (avocado)	0%	40° C	Benzyl alcohol	2
ozone control sample (avocado)	0%	40° C	Aniline	2
dry textured dyed with Dispersed Blue 3, Dispersed Blue 7	0%	40° C	Aniline	1
dry textured dyed with Dispersed Blue 3, Dispersed Blue 7	0%	40° C	Benzyl alcohol	2
dry textured dyed with Dispersed Blue 3	0%	40° C	Dimethyl formamide	2
dry textured dyed with Dispersed Blue 3	0%	40° C	Pyridine	1

Zero percent humidity was obtained by placing Drierite (anhydrous CaCO_3 with humidity indicator) on the bottom of the ozonizer chamber. The humidity was checked by an hydrometer placed in the chamber and by watching the color of Drierite.

Table 2

Exposure Experiments for Dyed Secondary Cellulose Acetate and
Cellulose Triacetate to Ozone Under Low Humidity

Substratum	Humidity	Temperature	Exposure time (hours)	Remarks
sec. Acetate, Triacetate, dyed with Blue 3 and with Blue 7, grey ozone fading con- trol (tri- acetate)	40%	40° C	22	
	0%-1%	40° C	22	substrata were put in dessi- cator for 1½ hours before exposure
	0%	40° C	23	1) heated to 80° C 2) put in dessicator for 4 days
ozone control (grey)	0%	45° C	6	

Exposures to Oxidants Other Than Ozone

1) Oxides of Nitrogen (NO_2)

Several experiments were performed in order to investigate whether NO_2 fades nylon carpets under high humidity (80% r.H.). NO_2 was generated in the ozonizer chamber by putting a bowl containing 3 grams sodium nitrite, 3ml phosphoric acid and 100 ml water, on top

of the water on the heated bottom of the chamber. A relative humidity of 80% was obtained and NO_x generated which was proven with the blue NO_x control ribbon. For these experiments the ozone producing bulbs were removed from the chamber.

2) Sodium Hypochlorite (NaOCl)

a) High concentration exposure:

Secondary cellulose acetate and cellulose triacetate dyed with 0.5% Disperse Blue 3 and 0.5% Disperse Blue 7 respectively were exposed to hypochlorite solutions with the following concentrations:

In 200 ml distilled water:

I 2 ml Clorox = 1% solution

II 1 ml Clorox = 0.5% solution

III $\frac{1}{2}$ ml Clorox = 0.25% solution

Clorox represents a commercial sodium hypochlorite solution with NaOCl content of 5.25%.

pH was raised to 9 for all three solutions by sodium hydroxide.

Exposure time: 22 hours.

temperature 20° C

liquor ratio 1:50

Three gram samples of steam textured nylon dyed with 0.5% Disperse Blue 3 and 1.5 gram samples of steam textured nylon dyed with 0.5% Disperse Blue 7 were exposed to sodium hypochlorite solution with the same concentrations and under the same conditions and exposure time as just described for secondary cellulose acetate

and cellulose triacetate.

b) Low concentration exposure:

A total of 11 grams of secondary cellulose acetate, cellulose triacetate, nylon dry textured, each one dyed with Disperse Blue 3 and Disperse Blue 7 respectively, together with ozone exposure standard for moist conditions (avocado carpet) and for dry conditions (grey triacetate fabric), were placed into 400 ml of ten parts per million available (Clorox) NaOCl solution. pH was adjusted to 8.0. Exposure time was 1½ weeks in the dark.

3) Hydrogen Peroxide (H_2O_2)

Secondary cellulose acetate, cellulose triacetate, nylon steam textured, each one dyed with Disperse Blue 3 and Disperse Blue 7 respectively were exposed to 3% hydrogen peroxide solutions (J. T. Baker, U.S.P.). Although only this one concentration (3% H_2O_2) was used, experiments adjusted to different pH values were performed. Liquor ratio was 1:50.

- I pH 6 exposure time 48 hours at 20° C
- II pH 12 adjusted with NaOH, exposure time 48 hours at 20° C
- III pH 12 adjusted with NaOH, heated to 70° C, exposure time
½ hour
- IV pH 10 adjusted with NH_4OH , exposure time 24 hours at 20° C

CHAPTER IV

RESULTS AND DISCUSSION

Ozone Fading of Dyes on Acetate Fibers

The results of ozone exposure of the triacetate series of fabric dyed with Disperse Blue 7 are shown in Table 3.

Table 3
Ozone Fading on 0.5% Disperse Blue 7 Dyeings on
Cellulose Triacetate Representing Different
Degrees of Accessibility

Cellulose Triacetate	Grey Scale Contrast	
	Dry Exposure	Moist Exposure
dyed (ring dyeing)	2	1
dyed, heat treated	4	3
dyed, with accelerant	3.5	2.5
dyed, with accelerant, heat treated	4	3

A direct comparison of the effect of ring dyeing versus well penetrated dyeing is shown herein. The ring dyeing as carried out under conditions which favor poor diffusion gave the most rapid fading change. In this case, evaluation of color differences was made visually

by reference to the international Grey Scale. A value of two is a severe change indeed on grey scale ratings, which are exponential rather than linear. Where penetration is obtained by use of higher energy conditions and/or use of a dyeing accelerant, a definite improvement is shown by the rating 3.5 and 4. The maximum resistance to ozone fading in this group of experiments is obtained by heat treatment. It is herein shown that the heat treatment, with its change of the internal fiber structure, gives a result beyond that of the value obtained where penetration is complete. A further observation is that even under the best conditions of good penetration of dye and of heat treatment, there remains still a susceptibility to ozone fading. This observation confirms the recommendation by Celanese in their Arnel Bulletin (TD 15 B) that presence of an ozone fading inhibitor is necessary to give the desired degree of ozone fading protection beyond the grey scale rating of 4.

The results obtained by exposure of the same series of samples to 20 parts per hundred million of ozone at high humidity (80%) suggest that accessibility of the fiber to ozone is an important factor in the rate of fading. The barely perceptible change shown by the grey scale value of 4 to the easily recognizable value of 3 represents a pronounced change. The effect of water here would be to swell the fiber, thereby making it more accessible to ozone absorption. Of course ozone does have significant solubility in water, and it can be argued that ozone is also absorbed by the water itself as well as by the swollen fiber.

In the experiments wherein the fading was carried out under conditions of very low humidity as obtained by placing Drierite on the

bottom of the chamber, the fading ratings were as follows: Secondary cellulose acetate dyeings with Disperse Blue 7 did not change noticeably. Cellulose Triacetate dyed with Disperse Blue 7 changed on exposure to a grey scale value of 2.5, which is less change compared to exposure at 25% relative humidity (Table 3).

A series of experiments was performed in which cellulose triacetate as well as secondary cellulose acetate dyed with Disperse Blue 3 and Disperse Blue 7 were given stepwise exposures. Cellulose triacetate dyeings for these experiments were made without accelerant and without subsequent heat treatment. The data of methanol extracts of exposed and unexposed dyeings are listed in Table 4 for Disperse Blue 3 and in Table 5 for Disperse Blue 7. The change in dye content of the substrata during exposure is also graphically presented for Disperse Blue 3 on Figure 3, for Disperse Blue 7 on Figure 4.

In the tables as well as in the figures, the dye concentrations are expressed in millimoles dye per kilogram fiber. Basis for the molarity of the dyes was an average molecular weight for the multi-component dyes. For Disperse Blue 3 the average molecular weight was found to be 303; for Disperse Blue 7 the average molecular weight was assumed to be 345.

One can see from the data presented in the tables that both dyes fade at a lower rate on secondary cellulose acetate than on cellulose triacetate. Both dyes fade equally slow on secondary acetate; only around 11% of the dyestuff is lost on this substratum after 48 hours ozone exposure. The fading rate on cellulose triacetate is higher.

Table 4

Data of Fading by Ozone of Secondary Cellulose Acetate and
Cellulose Triacetate Dyed with 0.5% Disperse Blue 3

Selected wavelength: 600nm, $k_{600} = 0.022$				
Methanol extract of 5 gram sample filled up to 100 ml, diluted with methanol as indicated				
	Absorption at 600 nm	Concen- tration gram/liter	Loss %	Dye content millimoles per kg
Secondary Cellulose Acetate, dilution 1:10				
Not exposed ⁺⁾	0.607	0.0134	-	8.04
12 h exp.	0.590	0.0130	3.0	7.80
24 h exp.	0.580	0.0127	5.2	7.62
36 h exp.	0.555	0.0122	9.0	7.32
48 h exp.	0.540	0.0119	11.2	7.14
Cellulose Triacetate, dilution 1:10				
Not exposed	0.500	0.0110	-	6.60
12 h exp.	0.425	0.0094	14.5	5.64
24 h exp.	0.387	0.0085	22.7	5.10
36 h exp.	0.343	0.0075	31.9	4.50
48 h exp.	0.315	0.0069	37.2	4.14

⁺⁾ Extrapolated

Table 5

Data of Fading by Ozone of Secondary Cellulose Acetate and Cellulose
Triacetate Dyed with 0.5% Disperse Blue 7

Selected wavelength: 620 nm, $k_{620} = 0.023$

Methanol extract of 5 gram sample filled up to 100 ml diluted with
methanol as indicated

	Absorption at 620 nm	Concen- tration gram/liter	Loss %	Dye content millimoles per kg
Secondary Cellulose Acetate, dilution 1:10				
Not exposed	0.437	0.0100	-	5.80
12 h exp.	0.430	0.0099	1.0	5.74
24 h exp.	0.420	0.0097	3.0	5.63
36 h exp.	0.396	0.0091	9.0	5.28
48 h exp.	0.388	0.0089	11.0	5.16
Cellulose Triacetate, dilution 1:5				
Not exposed	0.438	0.0101	-	2.93
12 h exp.	0.377	0.0087	13	2.52
24 h exp.	0.328	0.0075	25	2.17
36 h exp.	2.287	0.0066	34	1.81
48 h exp.	0.258	0.0059	41	1.71

Figure 3

Disperse Blue 3 Dye Content Versus Hours Exposure on
Cellulose Triacetate and on Secondary
Cellulose Acetate

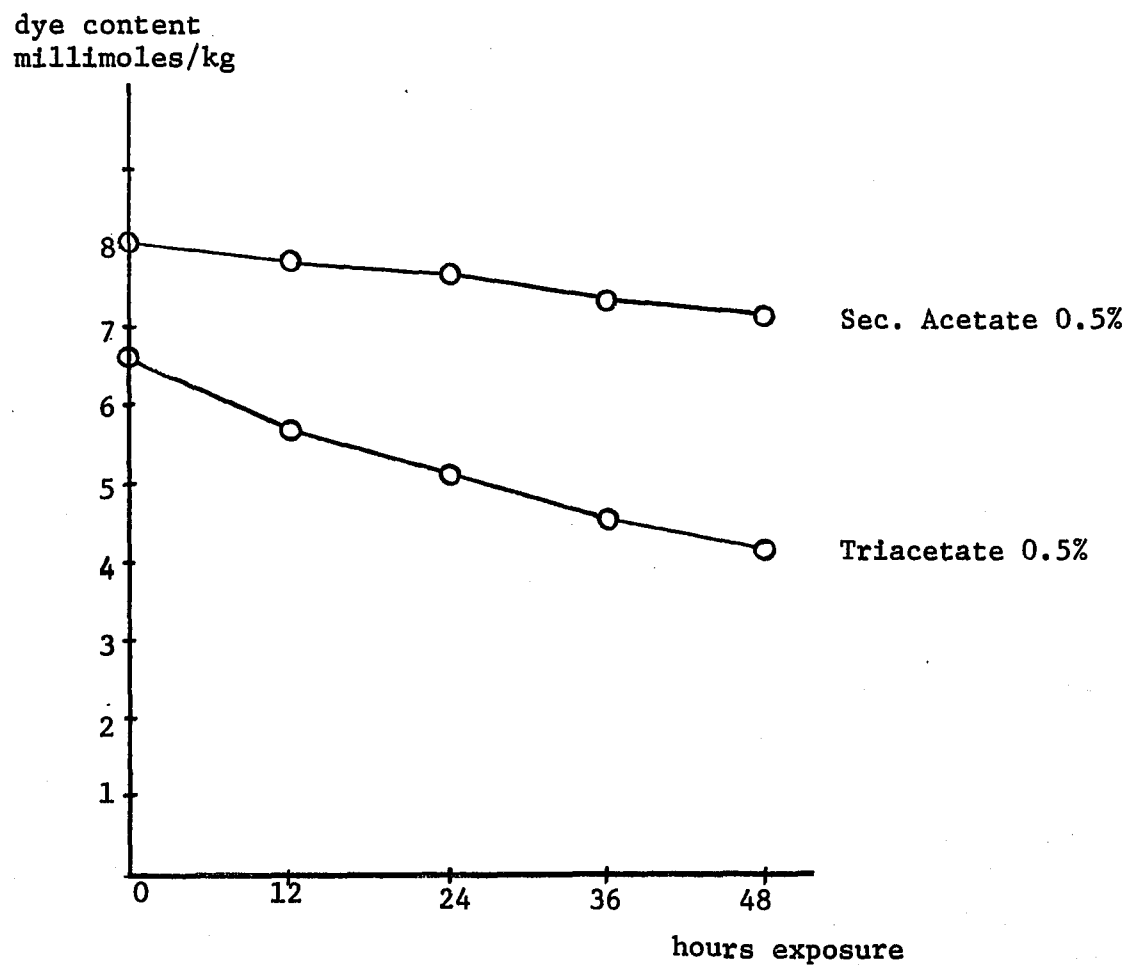
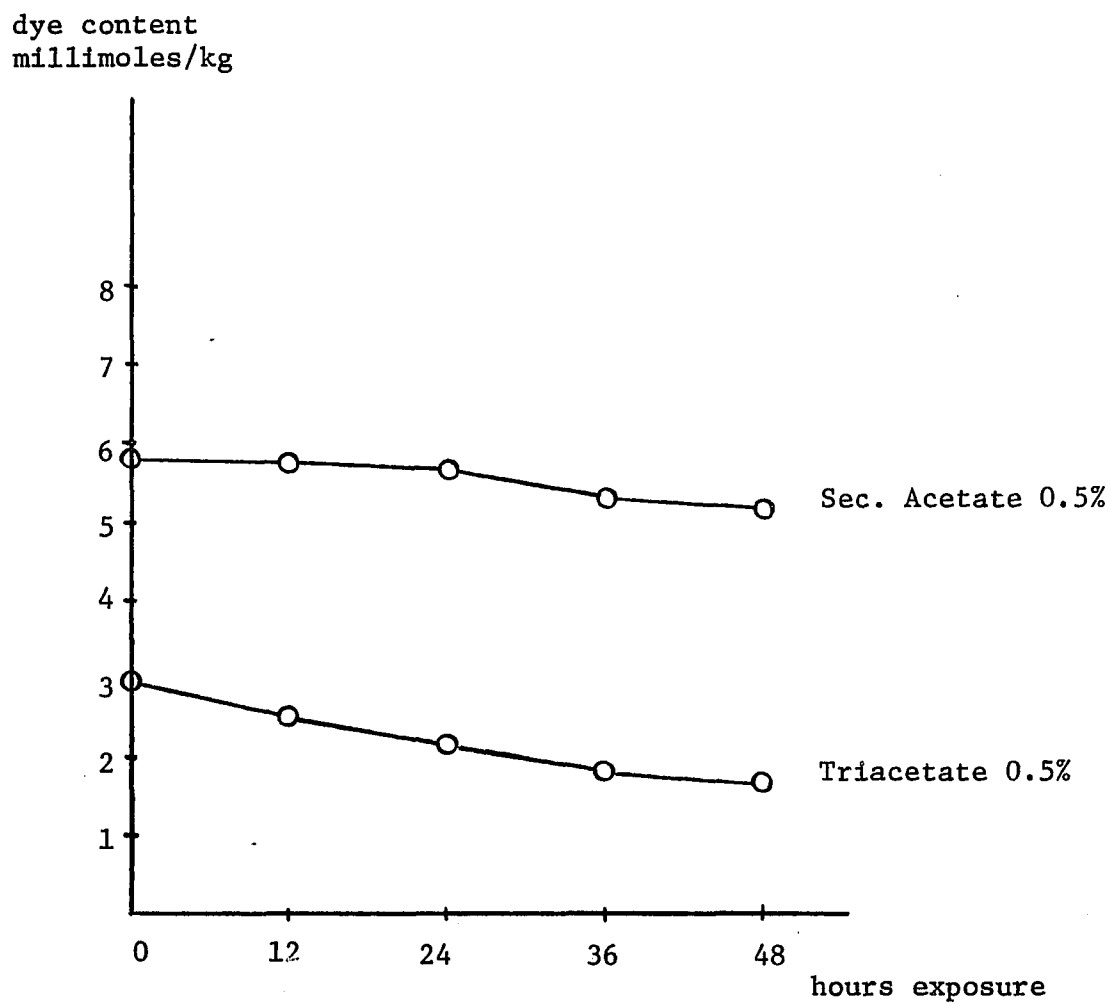


Figure 4
Disperse Blue 7 Dye Content Versus Hours Exposure on
Cellulose Triacetate and on Secondary
Cellulose Acetate



Disperse Blue 7 shows 41% loss of dye after 48 hours exposure while Disperse Blue 3 exhibits 37% loss of dye after 48 hours exposure. One would have expected that Disperse Blue 3 would fade faster since it fades more rapidly to other influences, such as oxides of nitrogen, ultraviolet light, and chlorine water, provided the dye is well penetrated throughout the fiber. Like in the first experiment; accessibility factors have to be considered to explain the obtained result.

Disperse Blue 7 exhibits a very slow dye diffusion rate, the diffusion rate of Disperse Blue 3 is considerably higher. According to Giles (31) and Giles and Rahmann (32), this is due to the aggregation tendency of Disperse Blue 7, which is caused by its two additional hydroxyl groups and the symmetry of its structure. Due to the high degree of crystallinity of cellulose triacetate it is very difficult for dyes to penetrate the fiber. Since a dye cannot penetrate crystalline regions, only regions of low order (amorphous regions) are available for dye sites. According to Weisz and Zollinger (33), even the low soluble disperse dyes are transported by an aqueous phase into hydrophobic fibers. With the use of e.g. dyeing accelerants the fiber swells and more regions become available through which the dye can move. After dyeing when the accelerant is removed and the swelling eliminated, the dye is restricted in its mobility. The restriction extends also to ozone which will have difficulties of reaching the dye through a tightly packed fiber structure until again a swelling state is produced.

Under the dyeing conditions used for the experiments described, a

ring dyeing was produced. With this the dye became absorbed mainly in regions which were readily accessible from the outside. Since no heat treatment after dyeing was performed which could have moved the positions of the dye molecules to regions of less accessibility, ozone fading occurred readily.

Disperse Blue 3 is able to penetrate cellulose triacetate slightly better than Disperse Blue 7, which explains the relative lower accessibility of the dye and higher resistance to ozone fading in this experiment.

It is not known how much ozone interacts with the fiber. A competitive reaction could take place whereby the chemical action of ozone becomes distributed between the fiber and the dye. It is known that surface saponification of triacetate which gives an outer cellulose layer by virtue of deacetylation results in a fiber structure which is completely resistant to ozone fading after dyeing. No explanation for this phenomenon has been offered. One might expect the cellulose layer to be a greater absorber of water and thereby facilitates fading because of greater absorptivity of ozone. However, it is shown by Bogaty, Campbell, and Appel (34) as well as by Katai and Schuerch (35) that cellulose does react with ozone and the cellulose layer may act as a protective barrier for this reason. Secondary cellulose acetate in this series of experiments is more resistant to ozone fading even when both the secondary cellulose acetate and the cellulose triacetate have well penetrated dyeings. A possibility exists here that the presence of hydroxyls in secondary cellulose acetate might be a site for some

ozone action. This hypothesis warrants further work.

Ozone Fading of Dyes on Nylon

In order to study the accessibility of the dye on nylon to the fading reactant and to interpret phenomena connected with ozone fading, rate studies were performed. The rate of reaction of ozone with the dye on nylon was studied by determining the change in concentration of the particular dye in the methanol extracts from exposed samples. Therefore only methanol extractable compounds could be observed in spectra taken from these extracts. In case of Disperse Blue 3 on nylon, a brownish degradation product remained on the fiber with the ozone exposed samples. Figure 5 and Figure 6 demonstrate spectra of methanol extracts for Disperse Blue 3 and Disperse Blue 7 on nylon exposed to ozone for different time periods under high humidity (80%). These spectra show that the maxima remained unaltered throughout fading, although there is a marked change in peak height due to the destruction of dye.

Both dyes do not fade on nylon when they are exposed to ozone under low humidity conditions. This previously known fact was also experienced in this investigation. Starting at approximately 70% relative humidity, both dyes fade, although at a very different rate. Disperse Blue 7 is resistant, whereas Disperse Blue 3 fades rapidly especially at the higher relative humidity of 80%.

The data of the rate study of nylon steam textured and dry heat textured for Disperse Blue 3 and Disperse Blue 7 are listed in Tables

Figure 5
Spectra of Methanol Extracts for Disperse Blue 3 on
Nylon Exposed for Different Time Periods

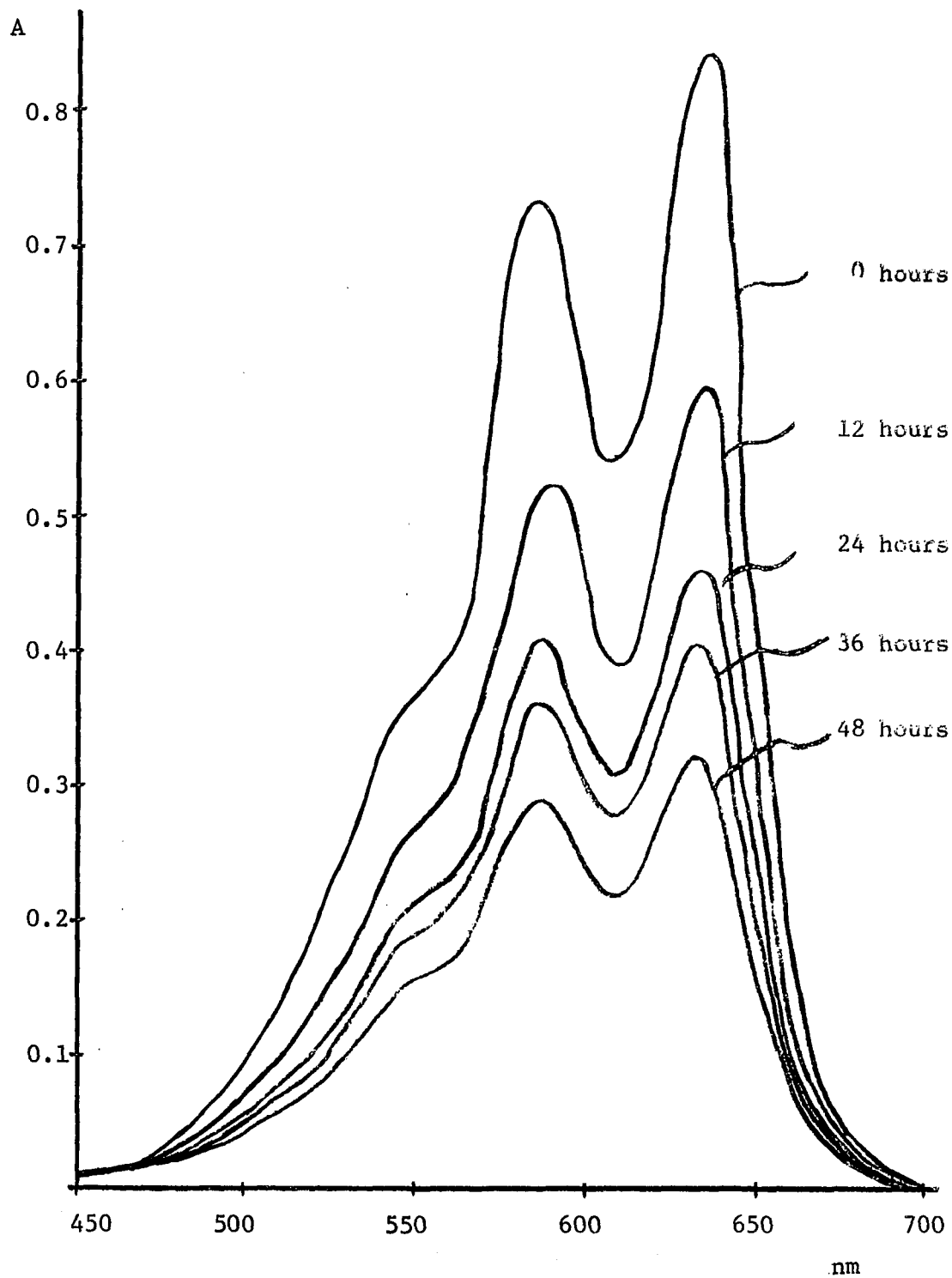
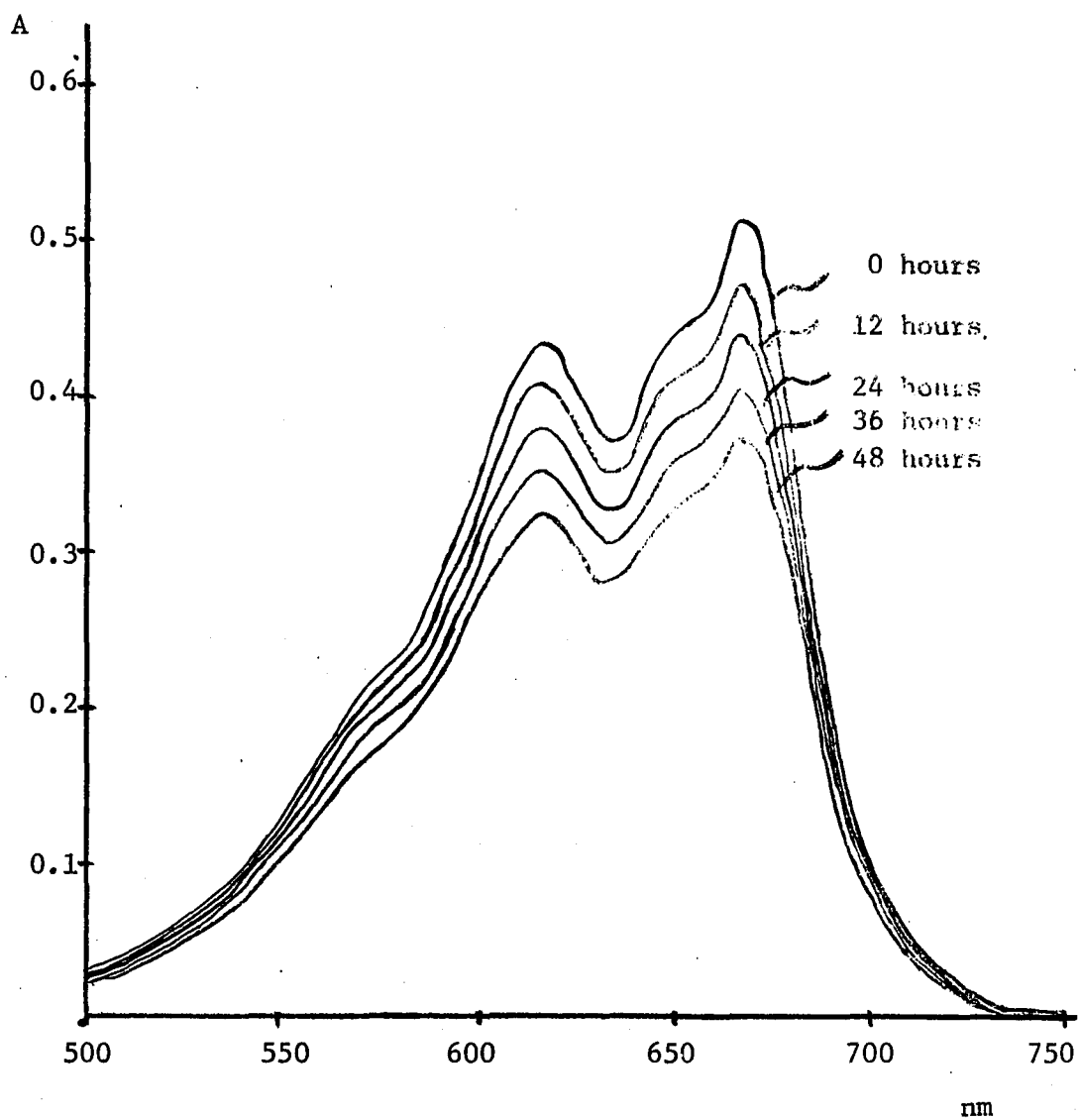


Figure 6
Spectra of Methanol Extracts for Disperse Blue 7 on
Nylon Exposed for Different Time Periods



6, 7, 8, and 9. The data are also presented as fading curves in Figure 7 for Disperse Blue 3 and in Figure 8 for Disperse Blue 7.

An attempt has been made to relate the obtained fading curves to rate equations in order to gain information on the reaction process. Especially of interest was whether the reaction for both dyes with ozone on nylon approaches a rate according to a first order law with respect to the dyestuff. A fading rate following a first order pattern would imply that each dye molecule in the substratum is equally accessible to the fading reactant. The kinetic picture thus obtained can only be regarded as a first approximation since only the dye is completely present at start of the reaction with the ozone reactant being fed. However, since the reaction has been followed by observing the dye concentration change, the results are believed to have significance. A kinetic interpretation is also complicated by the circumstance that commercial dyes were used for this investigation which are not uniform but consisting of several components. By using average molecular weight the concentrations in the rate study were expressed as millimoles dye per kilogram fiber.

If the reaction is first order with respect to the dye and c is the concentration of the dye, the rate can be expressed by:

$$\frac{-dc}{dt} = k \cdot c \quad (1) \quad \begin{array}{l} k = \text{rate constant} \\ t = \text{time} \end{array}$$

Thus, the rate of reaction with respect to disappearance of dye is only dependent upon the dye concentration present. By rearrangement of (1) the equation becomes

$$\frac{dc}{c} = -kdt$$

Table 6
Data of Fading by Ozone of Nylon Steam
Textured Dyed with Disperse Blue 3

Selected wavelength: 600 nm, $k_{600} = 0.022$

Methanol extract of 2.5 gram sample filled up to 100 ml,
diluted with methanol as indicated.

	Absorption at 600 nm	Concen- tration gram/liter	Gram dye on sample	Loss %	Dye content millimoles per kg
0.25% dyeing, dilution 1:2					
Not exposed	0.695	0.0153	0.00306	-	4.04
12 h exp.	0.554	0.0122	0.00244	20.2	3.22
24 h exp.	0.441	0.0097	0.00194	36.6	2.56
36 h exp.	0.375	0.0083	0.00166	45.8	2.19
48 h exp.	0.340	0.0075	0.00150	51.0	1.98
0.5% dyeing, dilution 1:5					
Not exposed ⁺⁾	0.510	0.0112	0.00560	-	7.40
12 h exp.	0.430	0.0095	0.00475	15.2	6.26
24 h exp.	0.338	0.0074	0.00370	34.0	4.89
36 h exp.	0.300	0.0066	0.00330	41.1	4.36
48 h exp.	0.240	0.0053	0.00265	52.7	3.50
2.0% dyeing, dilution 1:10					
Not exposed	0.728	0.0160	0.0160	-	21.10
12 h exp.	0.628	0.0138	0.0138	13.7	18.20
24 h exp.	0.553	0.0122	0.0122	23.8	16.10
36 h exp.	0.462	0.0102	0.0102	36.2	13.50
48 h exp.	0.396	0.0087	0.0087	45.6	11.50

⁺⁾ Extrapolated

Table 7
Data of Fading by Ozone of Nylon Dry Heat
Textured Dyed with Disperse Blue 3

Selected wavelength: 600 nm, $k_{600} = 0.022$

Methanol extract of 2.5 gram sample filled up to 100 ml, diluted with methanol as indicated.

	Absorption at 600 nm	Concen- tration gram/liter	Gram dye on sample	Loss %	Dye content millimoles per kg
0.25% dyeing, dilution 1:2					
Not exposed	0.764	0.0168	0.00336	-	4.43
12 h exp.	0.594	0.0131	0.00262	22.0	3.46
24 h exp.	0.498	0.0110	0.00220	34.5	2.90
36 h exp.	0.403	0.0089	0.00178	47.0	2.35
48 h exp.	0.370	0.0081	0.00162	51.8	2.14
0.5% dyeing, dilution 1:5					
Not exposed	0.574	0.0126	0.0063	-	8.31
12 h exp.	0.455	0.0100	0.0050	20.6	6.60
24 h exp.	0.400	0.0088	0.0044	30.2	5.81
36 h exp.	0.317	0.0070	0.0035	44.4	4.62
48 h exp.	0.282	0.0062	0.0031	50.8	4.09
2.0% dyeing, dilution 1:10					
Not exposed	0.746	0.0164	0.0164	-	21.60
12 h exp.	0.653	0.0144	0.0144	12.1	19.00
24 h exp.	0.555	0.0122	0.0122	25.5	16.00
36 h exp.	0.481	0.0106	0.0106	35.3	14.00
48 h exp.	0.400	0.0088	0.0088	46.4	11.60

Table 8
Data of Fading by Ozone of Nylon Steam
Textured Dyed with Disperse Blue 7

Selected wavelength: 620 nm, $k_{620} = 0.023$

Methanol extract of 2.5 gram sample filled up to 100 ml, diluted
with methanol as indicated.

	Absorption at 620 nm	Concen- tration gram/liter	Gram dye on sample	Loss %	Dye content millimoles per kg
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0.25% dyeing, dilution 1:2

Not exposed	0.513	0.0118	0.00236	-	2.74
12 h exp.	lost				
24 h exp.	0.466	0.0107	0.00214	9.3	2.48
36 h exp.	0.438	0.0101	0.00202	14.4	2.34
48 h exp.	0.389	0.0089	0.00178	24.6	2.07

0.5% dyeing, dilution 1:5

Not exposed	0.425	0.0098	0.0049	-	5.69
12 h exp.	0.400	0.0092	0.0046	6.0	5.34
24 h exp.	0.375	0.0086	0.0043	12.1	4.99
36 h exp.	0.348	0.0080	0.0040	18.3	4.64
48 h exp.	0.320	0.0074	0.0037	24.5	4.29

2% dyeing, dilution 1:10

Not exposed	0.894	0.0206	0.0206	-	23.90
12 h exp.	0.869	0.0200	0.0200	3.0	23.20
24 h exp.	0.825	0.0190	0.0190	7.7	22.10
36 h exp.	0.769	0.0177	0.0177	14.0	20.55
48 h exp.	0.738	0.0170	0.0170	17.5	19.70

Table 9
Data of Fading by Ozone of Nylon Dry Heat
Textured Dyed with Disperse Blue 7

Selected wavelength: 620 nm; $k_{620} = 0.023$

Methanol extract of 2.5 gram sample filled up to 100 ml, diluted
with methanol as indicated.

	Absorption at 620 nm	Concen- tration gram/liter	Gram dye on sample	Loss %	Dye content millimoles per kg
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0.25% dyeing, dilution 1:2

Not exposed	0.548	0.0126	0.00252	-	2.92
12 h exp.	0.464	0.0107	0.00214	15.4	2.48
24 h exp.	0.447	0.0103	0.00206	18.2	2.39
36 h exp.	0.440	0.0101	0.00202	19.8	2.34
48 h exp.	0.415	0.0095	0.00190	24.6	2.21

0.5% dyeing, dilution 1:5

Not exposed	0.420	0.0097	0.00485	-	5.62
12 h exp.	0.395	0.0091	0.00455	6.1	5.28
24 h exp.	0.385	0.0089	0.00445	8.2	5.16
36 h exp.	0.380	0.0087	0.00435	10.3	5.05
48 h exp.	0.345	0.0079	0.00395	18.5	4.60

2.0% dyeing, dilution 1:10

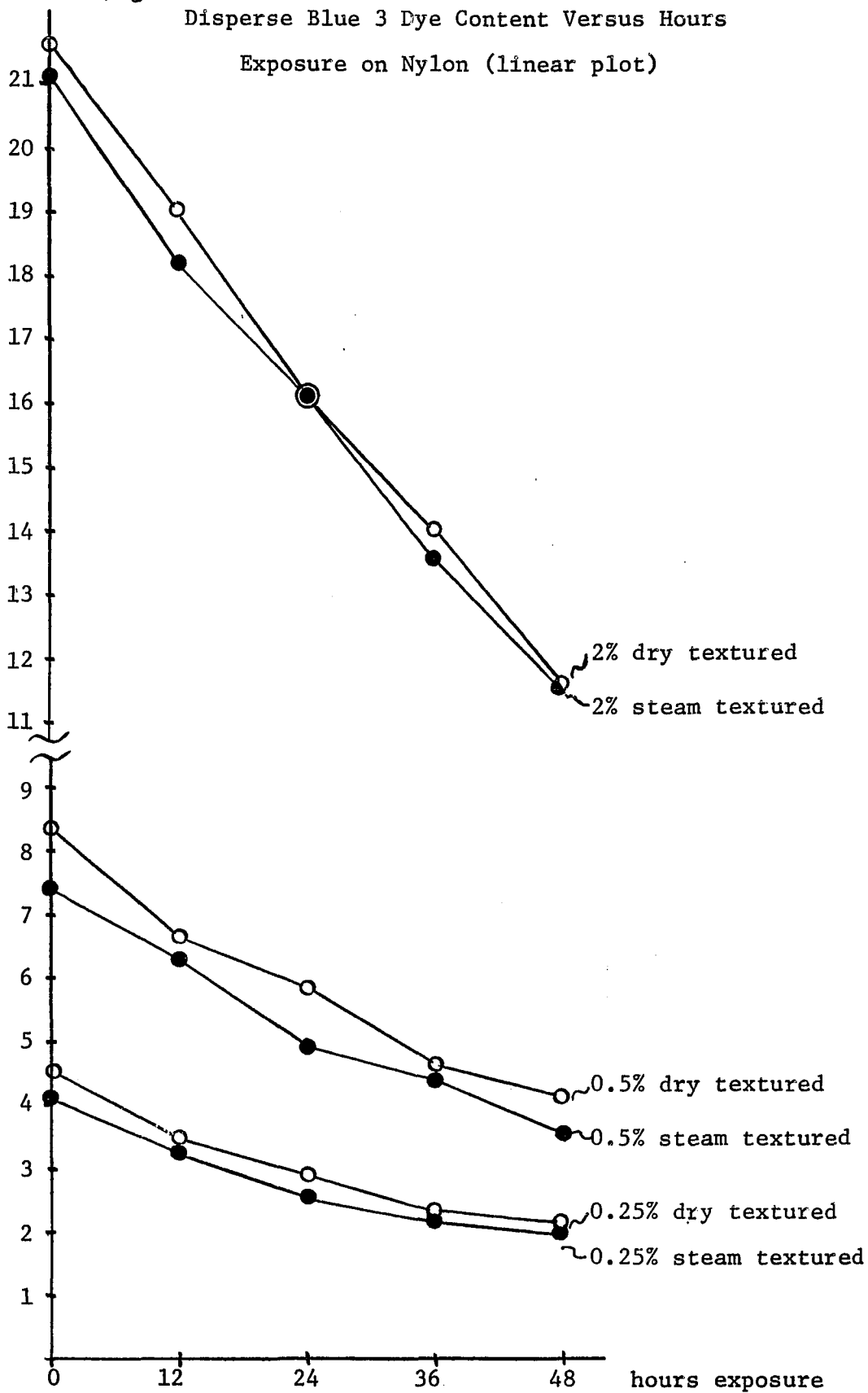
Not exposed	0.943	0.0217	0.0217	-	25.20
12 h exp.	0.925	0.0213	0.0213	2.0	24.70
24 h exp.	0.905	0.0208	0.0208	4.0	24.10
36 h exp.	0.865	0.0199	0.0199	8.2	23.10
48 h exp.	0.833	0.0192	0.0192	11.5	22.20

dry content
millimoles/kg

Figure 7

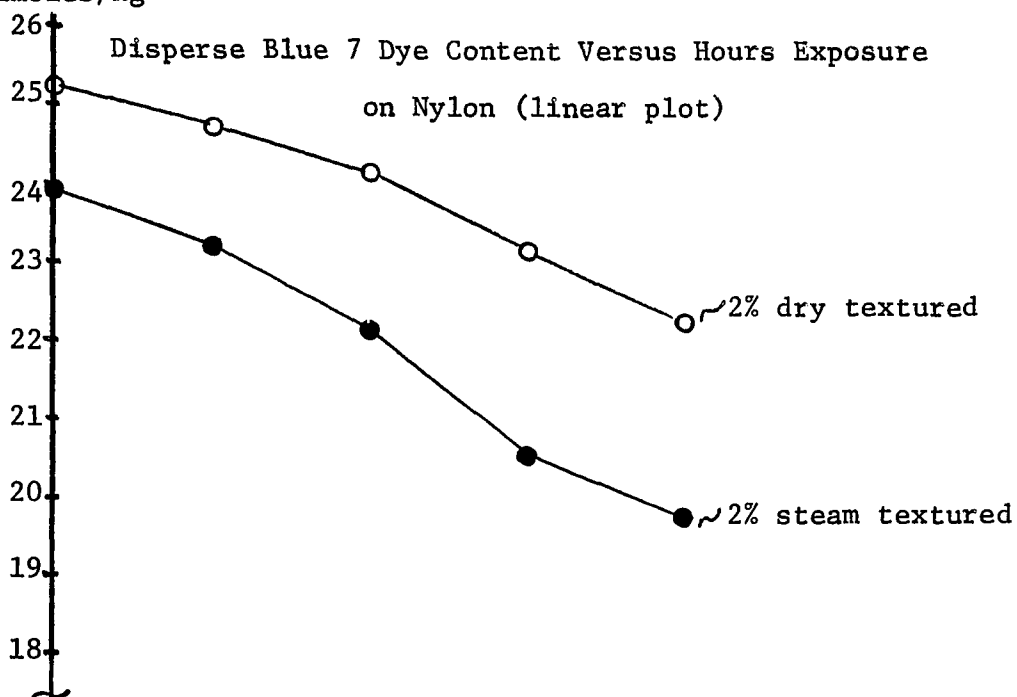
Disperse Blue 3 Dye Content Versus Hours

Exposure on Nylon (linear plot)



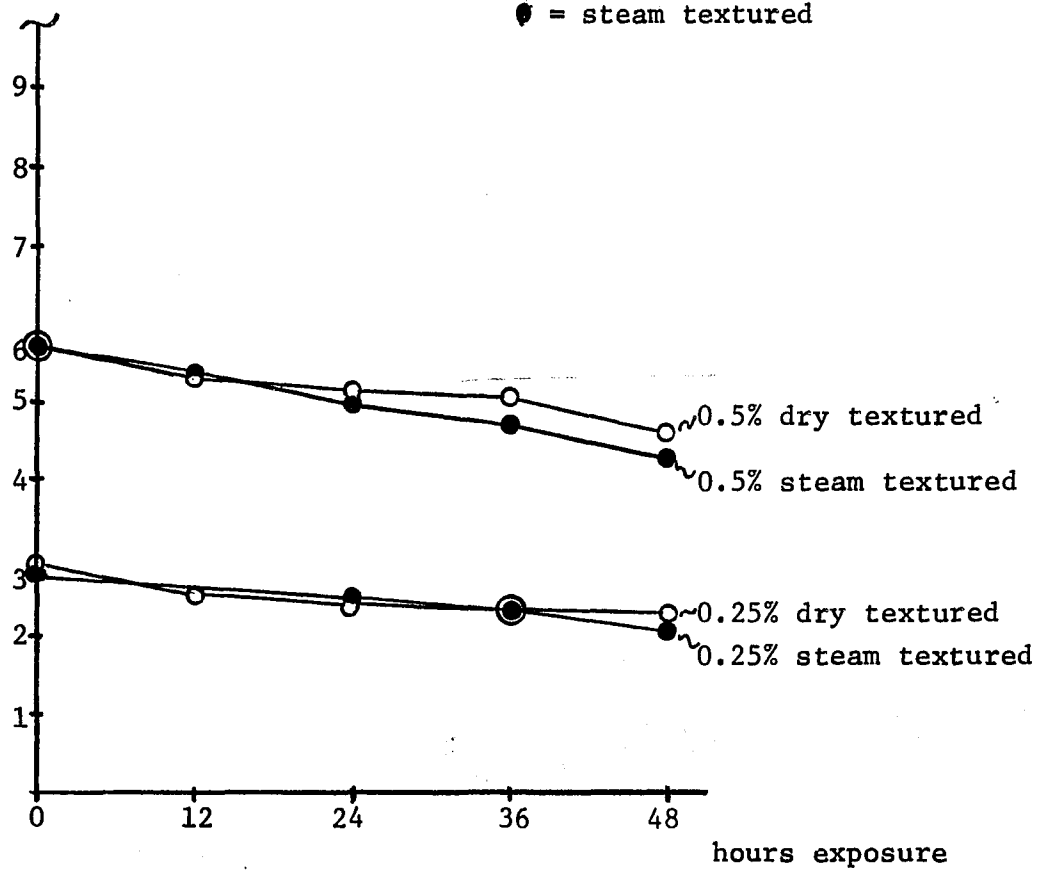
dye content
millimoles/kg

Figure 8



○ = dry heat textured

● = steam textured



and by integration

$$\ln c = -kt + C \quad (2)$$

Where C is the integration constant which in this case is the initial dye concentration. Hence, equation (2) can be written:

$$\ln c = \ln c_0 - kt \quad (3)$$

or

$$c = c_0 \cdot e^{-kt} \quad (4)$$

Equation (4) states that the rate decreases exponentially with time.

If the fading curves are exponential, a straight line should be obtained when they are plotted on a logarithmic scale. This was done in Figure 9 for Disperse Blue 3 and in Figure 10 for Disperse Blue 7. These two graphs show indeed that the ozone fading reaction for the two dyes on nylon follows an exponential rate pattern. In other words, each dye molecule in the dyeing must be equally accessible to ozone, which implies monolayer absorption state of the dye in the fiber or the presence of small aggregates where each dye molecule is still equally accessible.

The tendency of the dye to fade on the particular fiber under determined conditions is represented by the rate constant. In order to compare the tendencies of the dyes to fade, the rate constants of the fading reactions were calculated using equation (3) rearranged to (5).

$$k = \frac{\ln c_0 - \ln c}{t} \quad (5)$$

The calculated constants are listed in Table 10.

Figure 9

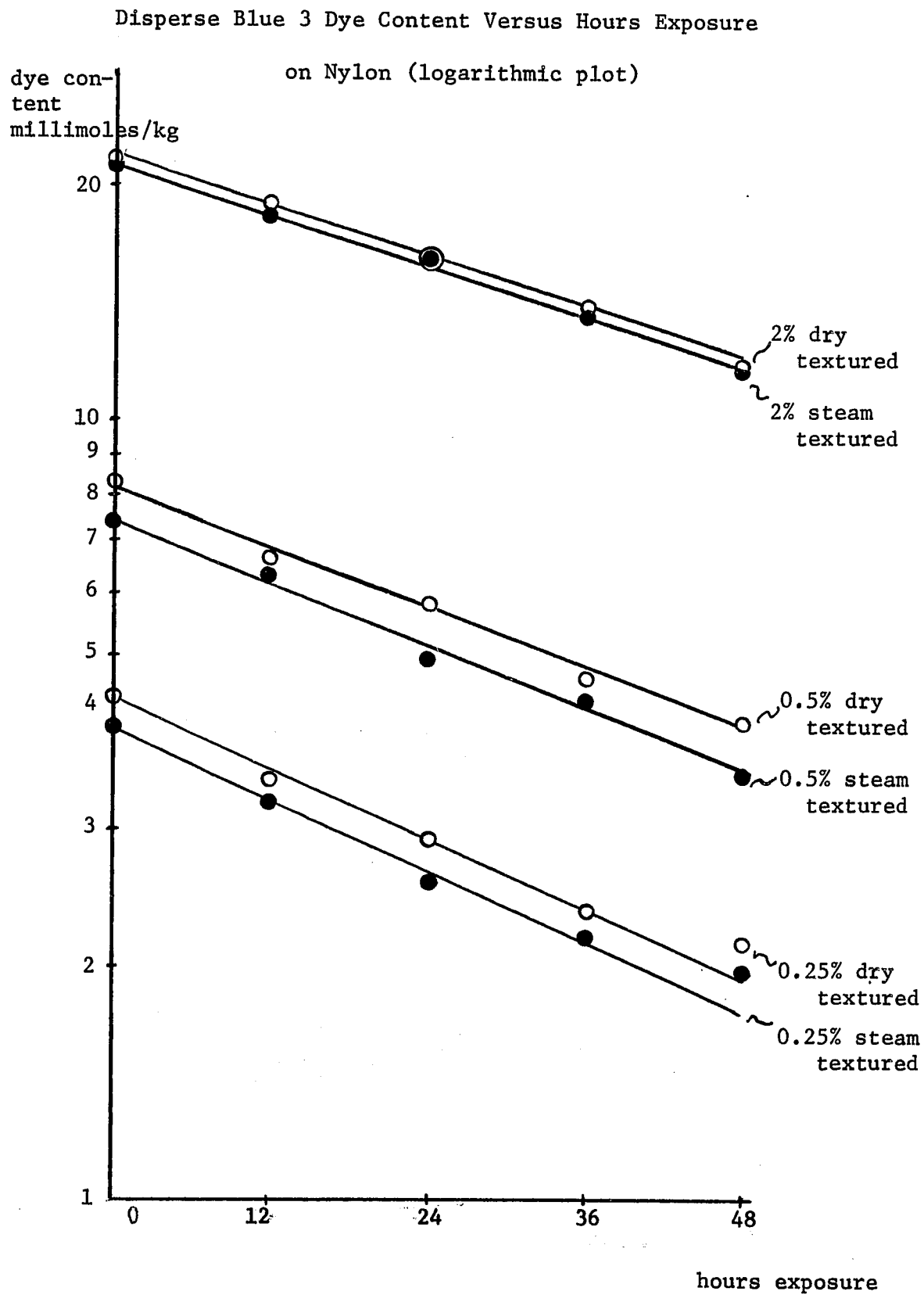


Figure 10

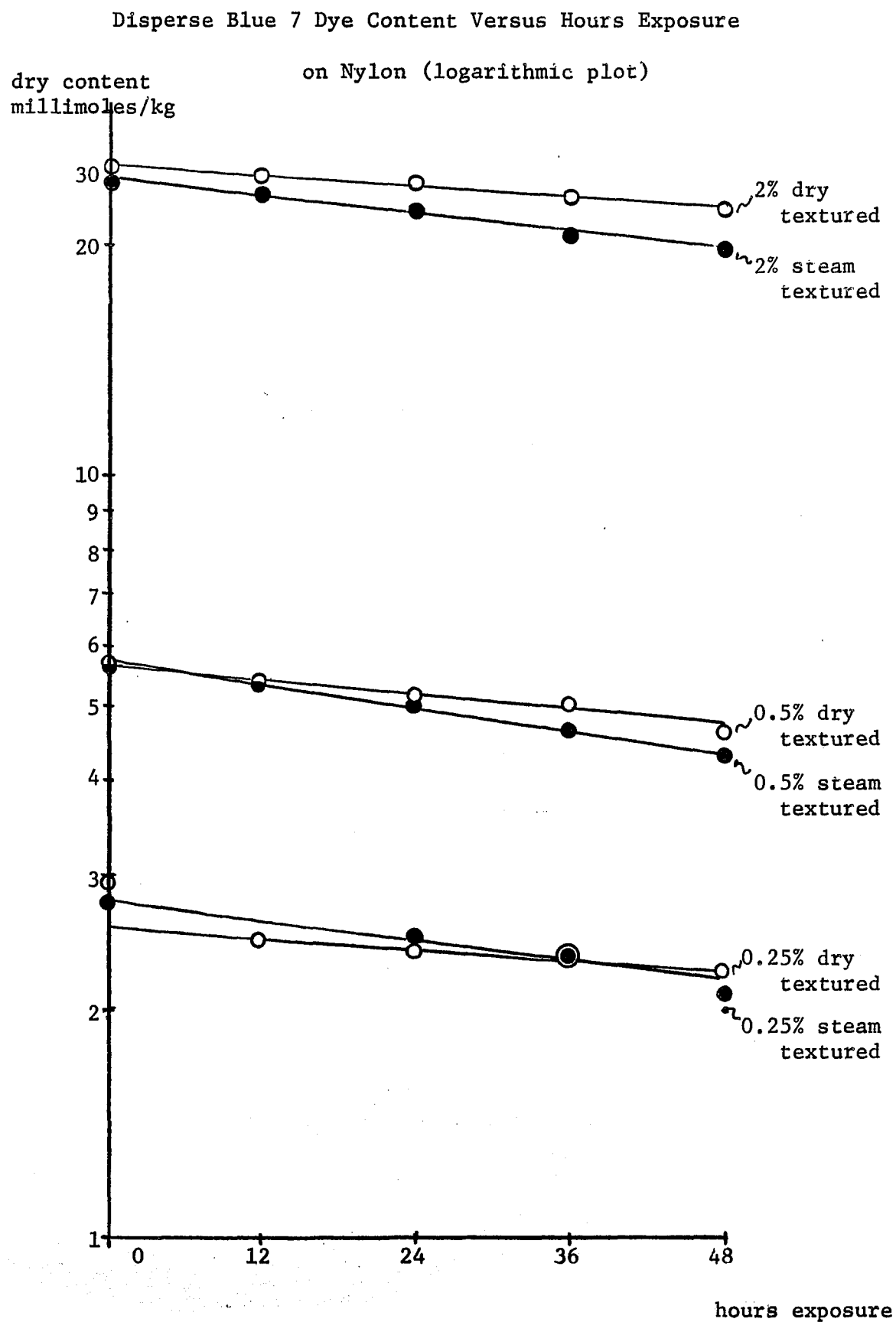


Table 10
Rate Constants of the Ozonization Reaction of
Disperse Blue 3 and Disperse Blue 7 on Nylon
Steam Textured and Nylon Heat Textured

Disperse Blue 3	Rate Constants 10^{-4} h^{-1}	
	Steam textured	Dry heat textured
0.25%	174	173
0.5%	160	154
2.0%	130	130
Disperse Blue 7		
0.25%	52	35
0.5%	60	35
2.0%	46	27

The rate constants show quantitatively the higher fading tendency of Disperse Blue 3 as compared to Disperse Blue 7.

Additional observations can be made from these rate constants:

- 1) The rate constants for the 2% dyeings are lower than for 0.25% and 0.5% dyeings.
- 2) There is no difference in the rate of fading between steam textured and dry heat textured nylon in case of Disperse Blue 3 dyeings; the fading rate of Disperse Blue 7 on steam textured nylon is different from that on dry heat textured nylon.

The rate constants for the 2% dyeings are lower probably due to a shift in the physical state of a dye with its concentration in the substratum. The dye becomes more associated as concentration increases. Giles, Johari, and Shah (36), who studied lightfading rates, also report for some dyes first order curves of successively falling rate constant, e.g. C. I. Disperse Red 11 (C. I. 62015) in polyester films. They state that the cause for this phenomenon is not clear.

The lack of difference in rate of fading between steam textured and dry heat textured nylon with Disperse Blue 3 is surprising. By the more open structure of steam textured nylon it should exhibit a higher fading rate compared to dry heat textured nylon. However, according to F. Taylor of Allied Chemicals, who supplied the nylon used in this study, moderate steaming in the texturing process with respect to temperature and time was applied. The differences in openness of structure were checked indirectly by wet bleeding tests and by "competitive dyeing" wherein the material with the easier dyeing properties will dye faster. Both tests revealed that there is almost no difference in accessibility between steam textured and dry heat textured nylon used in this study. As a consequence Disperse Blue 3 dyeings should exhibit similar fading rates. The difference in the fading rates with Disperse Blue 7 dyeings is thought to be due to its stronger absorption forces which can interact better with polymer structures of higher order. Even the slight difference between the molecular arrangement of dry heat textured and steam textured nylon used in this study seems to be significant for the difference in ozone fading of this dye. The reasoning

behind this statement is discussed next in connection with the interpretation of the observed difference in ozone fastness on nylon between Disperse Blue 3 and Disperse Blue 7.

Generally the factors governing the ozone fading reaction of dyes on textiles can be expressed as:

- 1) Interaction of dyestuff with ozone (reactivity of the dye)
- 2) Interaction of ozone with the fiber (accessibility of the dyed fiber)
- 3) Interaction of the fiber with the dyestuff (mode of attachment)

Each of the factors is influenced by the nature of the reaction partners and by the reaction conditions.

In order to interpret the different fading rate of Disperse Blue 3 and Disperse Blue 7 on nylon each of these factors has to be checked as to its relative contribution to the final picture.

The difference of interaction of dyestuffs with ozone was shown by Salvin and Walker (19), who established a relation between structure and color-fastness of disperse anthraquinone dyes to ozone. They showed that a reduction in the nucleophilicity of the amino nitrogen(s) in the amino anthraquinones reduces the degree to which these dyes are destroyed by the strongly electrophilic ozone. The structural difference between Disperse Blue 7 and Disperse Blue 3 is based mainly on the two additional hydroxyl groups in 5, 8 position with Disperse Blue 7. These two hydroxyl groups reduce the nucleophilicity of the substituted amino groups by favoring resonance structures yielding the corresponding immonium groups which are not

nucleophilic. This can account at least partly for the lower fading tendency for Disperse Blue 7 on nylon compared with Disperse Blue 3. However, the high fading rate of comparatively same magnitude for these two dyes on ring dyed cellulose triacetate points to the other factors as being responsible for the difference.

The interaction of ozone with the fiber can be of different kinds. The fiber can react with ozone and thereby exert inhibitor action, or it can restrict the accessibility to the dye sites. Since the dyes exhibit different fading rates when dyed on the same nylon substratum, an additional factor must be responsible for the difference in fastness to ozone.

The interaction of Disperse Blue 3 and Disperse Blue 7 with the fiber is definitely different due to the structural differences between these two dyes. Disperse Blue 7 is absorbed by nylon at a much lower rate than Disperse Blue 3. According to Vickerstaff (37) and many others, the attraction disperse dye-hydrophobic fiber is mainly polar in nature by formation of hydrogen bonds. Hydrogen bonds are also responsible for the solubility of the dye in water. Disperse Blue 7 with two more hydroxyl groups can be expected to be more soluble in water and more attracted by the fiber since more hydrogen bonds can be formed. However, it was noted that Disperse Blue 7 is less soluble than Disperse Blue 3. The reason for this phenomenon according to Giles (31) and Giles and Rahman (32) is the symmetry of the dye structure. They state that due to the symmetry there is apparently an increased difficulty for the individual molecule to break away from

the crystal structure to enter either the solution or the fiber. Giles also points out that anthraquinone dyes with a symmetry of substitution in the 1, 4, 5, 8 position, favor high light-fastness on polyester. It is believed by this author that the symmetry of Disperse Blue 7 accounts to some extent for the higher resistance of this dye to ozone fading in hydrophobic substrata where the dye has the opportunity to penetrate the fiber fairly well.

The reaction between the dye and the fading reactant requires collisions of the reaction partners. Not every collision leads to a reaction since some conditions have to be met:

- a) the reactants must collide on the reactive sites of the molecules
- b) with the collision the activation energy necessary for the reaction must be liberated
- c) this energy must be absorbed in a certain way

If all these conditions are met with the collision, the reaction takes place. Having these conditions in mind, it seems to be reasonable to relate fastness to ozone fading with the manner in which dyes are lodged in the fiber. In nylon, with its more or less ordered polymer structure, the symmetrical dye molecule once it gets in will arrange itself to this order and be kept quite rigidly. The chance is lower that such a dye molecule incorporated in this order is just in the right position relative to the attacking ozone or that it breaks away, gets dissolved into the swelling agent and collides with the fading reactant.

With respect to the difference in fading of Disperse Blue 7 in

steam textured and dry heat textured nylon, one can argue that the slightly more ordered polymeric structure of dry heat textured nylon provides better conditions for operating the symmetrically arranged proton donor-acceptor functions. For Disperse Blue 3 which compared to Disperse Blue 7 is not so symmetrical, the slight difference in the polymeric fiber structure in the used substrata is not critical.

Since high humidity is required for ozone fading to occur on nylon, it has been checked whether water enters into the reaction chemically. This was done by exposing dyed nylon to ozone under low or without humidity but impregnated with organic solvents. The result was that ozone control samples (avocado nylon carpet) faded dramatically at 3% and 0% humidity when impregnated with benzyl alcohol. The sample turned orange after only 24 hours of exposure, which is much faster than with the high humidity exposure. This avocado shade is dyed using Disperse Blue 3 as the blue component. Dry textured nylon used in this work and dyed with Disperse Blue 3 faded strongly without humidity and impregnated with benzyl alcohol. Under the same conditions, Disperse Blue 7 did not fade much, which is in line with its behavior under high humidity.

Fading under low (4%) humidity also occurred with the ozone control sample and Disperse Blue 3 dyed steam textured nylon, using dimethylformamide for impregnation. The fading obtained, however, was much lower than the one obtained using benzyl alcohol. Benzyl alcohol and dimethylformamide are recognized swelling agents for nylon. Exposure experiments with dry textured nylon, dyed with Disperse Blue 3

and Disperse Blue 7, as well as with the ozone control sample, under 0% humidity and impregnated with pyridine and aniline did not result in fading. The reason for the negative result could be that nitrogen containing organic solvents act as inhibitors. A negative result was also obtained with benzene as impregnation agent probably due to its volatility and low swelling action.

Since water can be replaced by organic solvents which absorb ozone it can be concluded that water does not enter the fading reaction chemically of dyes on nylon.

Another question is whether water is the vehicle for ozone to the dyestuff absorbed within the fiber and whether water within the fiber is the reaction medium.

Under high humidity exposure conditions the nylon material approaches the swelling state it had during the dyeing process. Thus the regions where the dye is located become accessible to the fading reagent. With the swollen nylon material the available absorptive fiber surface is covered with water. In order to become directly absorbed to the fiber polymer ozone would have to displace the already absorbed water. It is more likely that the water in the fiber acts as an absorbent for ozone and as a vehicle to the dyestuff.

Fading of Dyes by Oxidants Other Than Ozone

The results of the experiments performed with sodium hypochlorite and hydrogen peroxide as oxidants showed quite a similarity to ozone fading. The same accessibility criteria seem to be valid. Ring

dyed cellulose triacetate was affected most and equally for both Disperse Blue 3 and Disperse Blue 7. Secondary cellulose acetate suffered moderate changes, again both dyes faded equally. Marked changes were observed for Disperse Blue 3 on nylon whereas for Disperse Blue 7 only slight fading occurred. Fading caused by hydrogen peroxide was not as pronounced as with sodium hypochlorite but the changes were at least visually of the same kind. Generally the fading shades obtained with the exposures to sodium hypochlorite and hydrogen peroxide were the same as for ozone exposure. A loss of color rather than discoloration occurred.

It is well established that oxides of nitrogen, which are oxidative in nature, produce a red colored degradation product with several disperse blue dyestuffs, e.g., with Disperse Blue 3 on secondary cellulose acetate. This red color does not appear with the same dyes on cellulose acetate exposed to ozone. This visible difference between these two fading reactions is probably due to nitrosation reactions of NO_2 with the dye, which does not occur with ozone. Although NO_2 is not considered to be a fading agent of actual significance for nylon carpets, it was checked whether NO_2 is able to fade such a material under the same conditions as ozone. Avocado ozone control samples were exposed to NO_2 under 80% humidity. With this exposure the material faded strongly to the same yellow color typical for ozone fading.

Analysis of Reaction Products

The components of the dyestuffs used in this investigation and degradation products formed with ozone exposure of these dyes on the different substrata, were isolated and some of them analyzed. Many degradation products are only present in minute quantities after the reaction is stopped, which made their analysis difficult or even impossible with the experimental facilities available for this study. Minute quantities of certain degradation products do not necessarily mean that their presence is of no importance. Some of them might be important intermediates; the knowledge of their presence and their structure could provide valuable information for the investigation of the mechanism involved.

Before degradation products can be studied the undegraded components of the dyes have to be known. Thin layer chromatograms were made of the dyes used and the R_f values determined in order to recognize undegraded dye out of more complicated chromatograms made from exposed dye. For Disperse Blue 3 (GAF) the R_f values are listed in Table 11, for Disperse Blue 7 (Sandoz) in Table 12. It must be emphasized that the R_f values in this investigation are significant only in their relative magnitude but not in their absolute numbers. The reason for this is that the silica gel which was used from three different lots differed considerably in its absorption power.

Table 11

 R_f Values of Disperse Blue 3 Using 1 mm Adsorbosil

Covered Plates and n-Hexane: Acetone 7:3

as Mobile Phase

Band (Spot) number	Appearance	R_f Value
1	blue, strong	0.63
2	blue, strong	0.59
3	blue, strong	0.55
4	violet, faint	0.51
5	violet, faint to weak	0.47
6	purple, weak	0.38

Table 12

 R_f Values of Disperse Blue 7 Using 1 mm Adsorbosil

Covered Plates and Benzene: Acetone 4:1

as Mobile Phase

Band (Spot) number	Appearance	R_f Value
1	faint, diffuse	0.83
2	faint, diffuse	0.67
3	weak	0.50
4	weak	0.43
5	faint, diffuse	0.33
6	reddish blue, strong	0.23
7	greenish blue, strong	0.05

The components of Disperse Blue 3 were identified by infrared spectroscopy, by comparison with standard spectra, as:

Band no. 1	1,4-bis-(methylamino) anthraquinone
Band no. 2	1-methylamino-4-hydroxyethylamino anthraquinone
Band no. 3	1,4-bis-(hydroxyethylamino) anthraquinone
Band no. 4	Derivatives of 1-alkylamino-4-hydroxyanthraquinone
Band no. 5	
Band no. 6	

The two main components of Disperse Blue 7 looked very similar in the infrared spectrogram.

Band no. 7 1,4-bis-(hydroxyethylamino) 5-,8 dihydroxyanthraquinone

Examining the chromatograms of extracted dyes which were exposed to ozone on different substrata for different times some features of the reaction can be visualized, Figure 11 shows a chromatogram of Disperse Blue 3 exposed on cellulose triacetate for 0, 12, 24, 36, 48 hours. As one can see; spot no. 6 disappeared already with 12 hours exposure. Spot no. 4 and 5 became weaker with exposure time but this is in line with the reduction in concentrations of bands 1, 2, 3. A new red spot appeared between spot no. 4 and no. 5. (which cannot be seen clearly on this photograph). The spotting area contained a compound which did not move with the mobile phase used. This compound increased in concentration with exposure time and can be considered as one of the final degradation products.

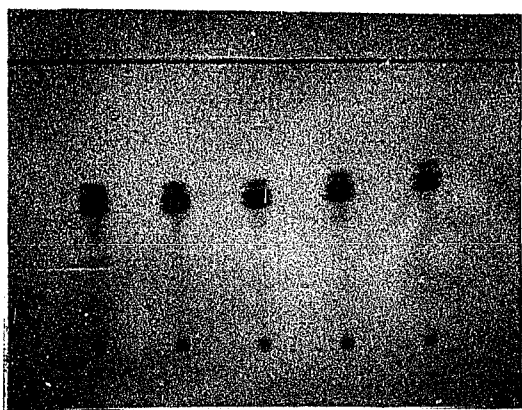
The same dye exposed on nylon exhibited a chromatogram which differed in some detail from the one with the dye exposed on triacetate

(Figure 12). Spot no. 6 disappeared more gradually with exposure time compared with Figure 11. It took 36 hours for this compound to disappear. The spotting area looks pretty much the same; no increase in concentration can be seen. The reason for this is that this compound remains on nylon and is not extractable with methanol.

The chromatogram of Disperse Blue 7 exposed on triacetate is pictured in Figure 13. Generally the concentration of the spots became weaker with exposure time except for a compound in the spotting area which again is not moving and which became more concentrated with exposure time. There was also a new red compound appearing, first visible with the 24 hours exposure and getting more concentrated with longer exposure time.

Disperse Blue 7 exposed on nylon seemed not to change much; the chromatogram (Figure 14) exhibited almost no difference between the spots of dye with different exposure time.

In the chromatograms of exposed Disperse Blue 3 it was striking that spot no. 6 disappeared first. Further, that spot no. 6 disappeared at a different rate with exposure on triacetate and no nylon. Since no major colored degradation product appeared in the chromatograms of Disperse Blue 3 exposed on both triacetate and nylon, except the final product in the spotting area, it was hypothesized that the structure of spot no. 6 is at the same time an intermediate in the fading reaction. This intermediate is not present at a higher concentration in these chromatograms, because the rate of reaction with ozone of these species is high. In order to arrive at some



0 12 24 36 48

Figure 11

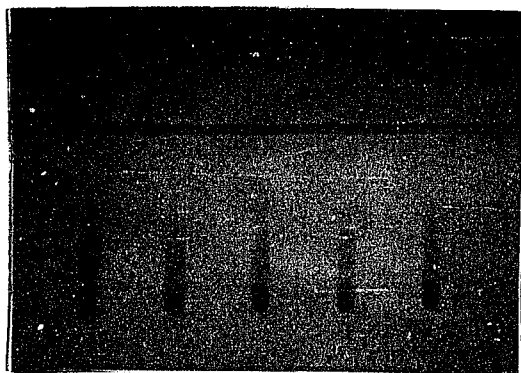
Chromatogram of Disperse Blue 3
Exposed on Cellulose Triacetate



0 12 24 36 48

Figure 12

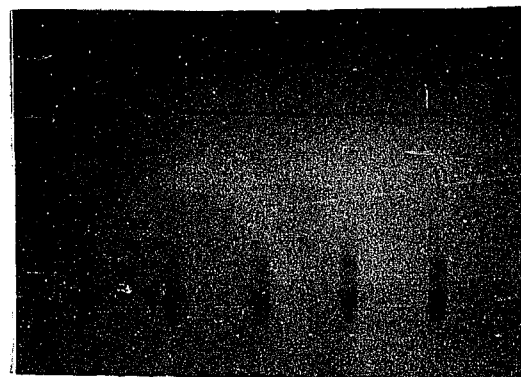
Chromatogram of Disperse Blue 3
Exposed on Nylon



0 12 24 36 48

Figure 13

Chromatogram of Disperse Blue 7
Exposed on Cellulose Triacetate



0 12 24 36 48

Figure 14

Chromatogram of Disperse Blue 7
Exposed on Nylon

indications that this hypothesis can be correct the following experiment was performed: Thin layer plates were spotted (streaked) with Disperse Blue 3, and developed in order to get the compounds separated. The plates, with the separated compounds still on, were exposed to moist ozone for 23 hours. After exposure the band no. 1, 2, 3 (main bands) were scratched off separately and separated from the silica gel in the described manner (chapter "Procedures"). These exposed bands were spotted on new thin layer plates and again developed in order to see the formed degradation products of each band. The following bands were obtained from this experiment (Table 13):

Table 13

Degradation Products of Band 1, 2, 3 (Disperse Blue 3)

Exposed to Ozone on Silica gel

Band No.	Appearance	R_f	Original Band No.		
			1	2	3
1	blue, strong	0.49	p		
2	blue, strong	0.46		p	
3	blue, strong	0.43			p
a	pink, weak	0.41	p	p	p
5	weak	0.35	p	p	p
b	yellow, very faint	0.32	p	p	p
6	purple, strong	0.26	p	p	p
c	purple, faint	0.08	p	p	p
Streak area		0.00	p	p	p

p = present

R_f values obtained on these chromatograms differ widely from R_f values of the same compound on previous chromatograms. A new lot of silica gel was used which differed widely in its absorption power from the older lot. A factor of approximately 1.3 - 1.45 transforms this R_f values to R_f values of the old lot.

A purple band with the relative position of band no. 6 of the original dye is present on the chromatograms of each exposed band. In order to check the identity this band was scratched off, separated from silica gel and analyzed by measuring the infrared absorption. This newly formed compound was found to be identical with the compound in band no. 6 of the original dye.

The fading pattern of a thin layer plate is quite different from that of a textile substratum. By using these quickly covered plates one can see layers of degradation products with different degrees of degradation down to the original dye still present in layers close to the glass plate. Maybe because of this profile of reactant accessibility the purple intermediate had a greater stability compared to its situation on the ring dyed cellulose triacetate.

The reaction intermediate represents a compound which differs from the original dye in the lack of one secondary amino groups which has been replaced by a hydroxyl group. The reaction pattern leading to this intermediate would point to the amino nitrogen of the anthraquinone nucleus as the principal point of oxidative attack. This would also correspond to the observation of Salvin and Walker (20) with respect to the relation between nucleophilicity of the amino group

and the tendency to fade of amino anthraquinone dyes.

Extracts of Disperse Blue 3 dyeings on secondary cellulose acetate and cellulose triacetate, exposed to ozone for 110 hours were analyzed. The degradation products were separated by thin layer chromatography; the bands which were either visible by their color or by their fluorescence under ultraviolet light were scratched off and separated from silica gel. Infrared spectroscopic examination of the separated compounds revealed as final degradation product derivatives of phthalic acid.

The possibility for the formation of phthalic acid by action of strong oxidizing agents on anthraquinones is mentioned in the book "Anthracene and Anthraquinone" by Barnett (38). He states on page 20:

Anthraquinone is a very stable substance and resists the action to oxidizing agents to a very marked extent.

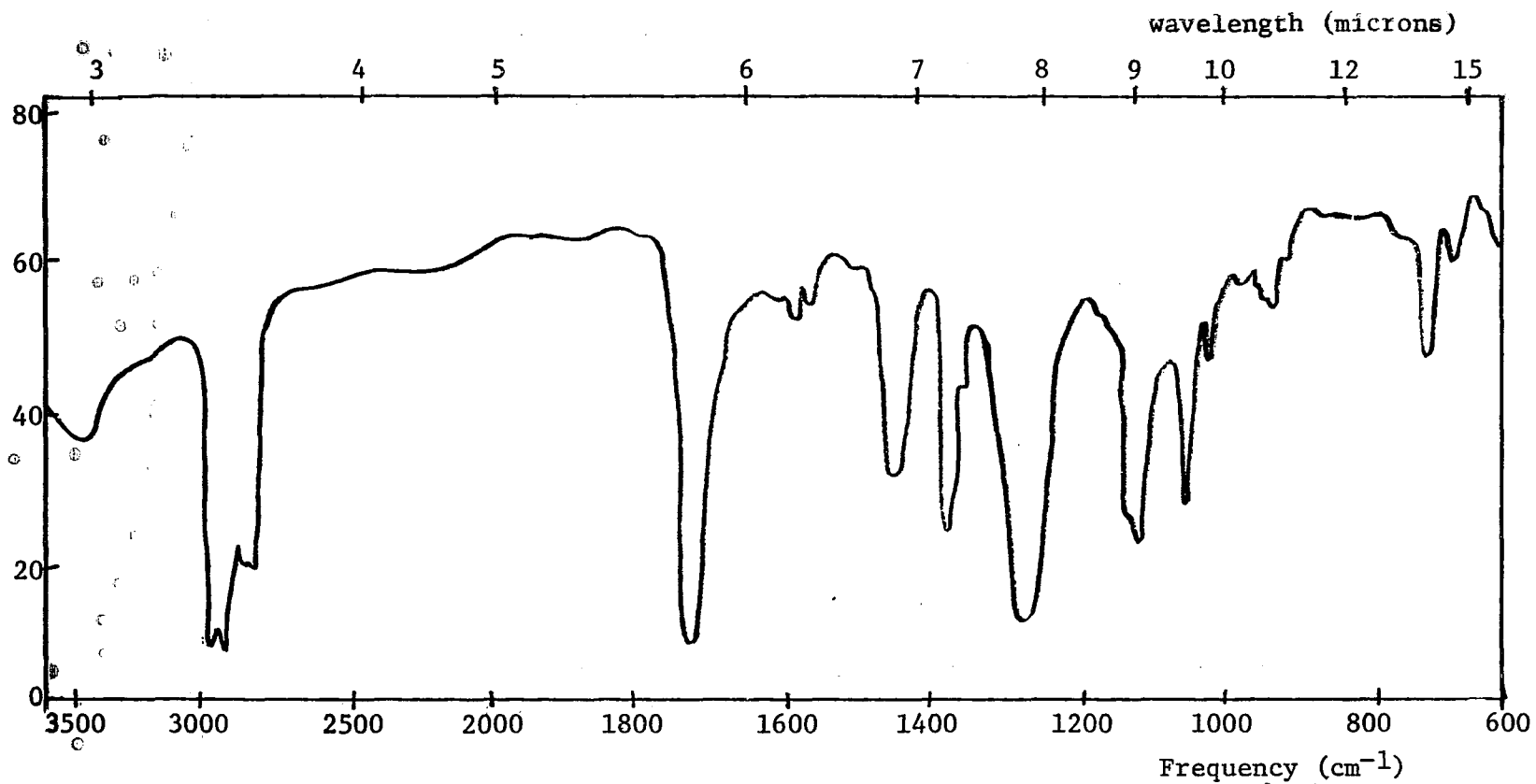
and further:

If only one of the benzene rings is weakened by the presence of hydroxyl or amino groups, it will be possible to obtain phthalic acid from the substance.

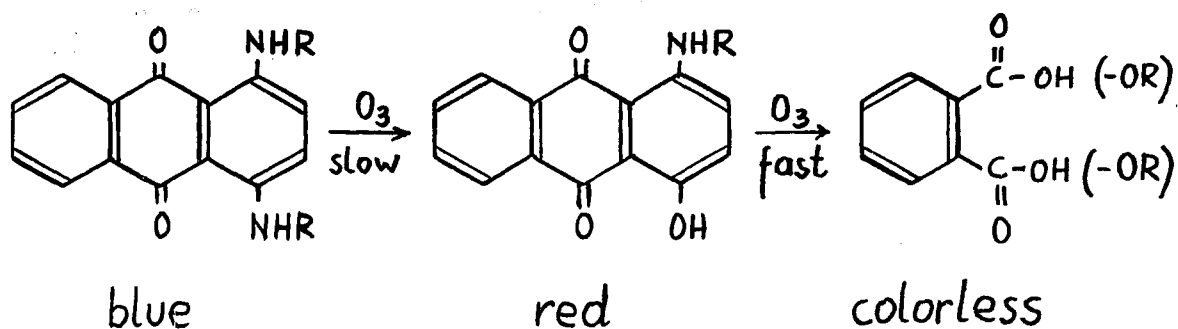
One of the infrared spectra obtained from an ozone degradation product of Disperse Blue 3 is shown in Figure 15. By comparison with similar spectra found in Sadtler Catalog of Infrared Spectrograms (30) this spectrum was interpreted as an ester of phthalic acid, probably the methyl, ethyl ester. No profound explanation was found why an ester is formed.

Figure 15

Infrared Spectrum of Dye Degradation Product



Schematically the ozonation reaction of Disperse Blue 3 on the fiber appears to take place as follows:



The formation of phthalic acid derivatives as final degradation products makes it plausible that loss of color rather than shade change is observed with ozone exposure of Disperse Blue 3 dyed textiles.

A similar reaction path is anticipated for Disperse Blue 7.

CHAPTER V

SUMMARY AND CONCLUSIONS

The action of ozone in causing fading of vulnerable dyes can be shown as dependent on two major factors:

- a) Accessibility of the fiber to ozone
- b) The availability of the dye for chemical reaction with ozone

Although ozone has a fading effect on azo dyes, its action is most pronounced on red and blue anthraquinone dyes.

The action of ozone is to cause destruction of the chromophore thereby giving a loss of color rather than shade change. Whereas oxides of nitrogen gives shade change of blues to reds by attack on the auxochrome groups (amino and alkylamino), the action of ozone is to give a deep seated decomposition of the anthraquinone chromophore with resulting formation of colorless or very slightly yellow compounds. This was demonstrated by methanol extraction of ozone exposed dyeings of Disperse Blue 3 on cellulose triacetate and nylon 6. The extract was separated by thin layer chromatography and the separated components examined by infrared spectroscopic means. The products of ozone fading of Disperse Blue 3 (1, 4-dialkylamino anthraquinone) were found to be derivatives of phthalic acid. This suggests that ozone has attacked the anthraquinone system with rupture of one of the rings.

The rate of fading of the dyes by ozone is related to the ease with which ozone is absorbed and diffuses to the dye sites. The

absorption rate of ozone varies with the openness of fiber structure. With fibers of close packing and highly crystalline nature, the ozone fading rate is low. This is shown in the cellulose triacetate series, where increased crystallinity obtained through heat treatment at 200°C is accompanied by increased resistance to ozone fading.

It is known that higher resistance to ozone fading on nylon 66 is obtained when the nylon is textured by dry heat rather than by steam. Comparison of the fading rates of nylon 6 dry heat textured versus steam textured did not show the expected differences. By means of competitive dyeings tests (inward diffusion) and by wet bleeding tests (outward diffusion), on the steam and dry heat textured nylon 6, no significant differences in openness of structure could be demonstrated. With no differences in openness of structure the lack of difference in ozone fading rate is logical.

The accessibility factor in ozone fading is further shown in the effect of humidity in fading of nylon 6. Nylon 6 dyed with Disperse Blue 3 resists action of ozone when exposed at humidities up to 65% r.h. At higher humidities, 70-90%, there is pronounced fading as shown in the high humidity ozone fading chamber constructed according to principles of AATCC Test 129-1968. The effect of high humidity is to cause swelling of the fiber, pushing apart the fiber molecules and thereby permitting greater accessibility with increased inward diffusion of ozone.

The swelling action of water can be duplicated by using alternative organic solvents for swelling action. Thus benzyl alcohol and dimethylformamide used as potential swelling agents acted to give increased

fading after impregnation. Benzyl alcohol proved superior to dimethylformamide in its accelerating action and this correlates with the known superior swelling action of benzyl alcohol upon nylon 6. (Benzyl alcohol is used as a swelling agent in equalizing the differential dyeing of barre^l susceptible nylon.)

On cellulose triacetate, a ring dyeing prepared by use of low dyeing temperature in absence of dyeing accelerant, shows more rapid fading than well penetrated dyeing using recommended higher dyeing temperature (95°C) and the dyeing accelerant trichlorobenzene.

Dyes on secondary cellulose acetate fade at a lower rate than on cellulose triacetate. Due to the open structure of secondary cellulose acetate one might expect a more rapid fading rate. The reasons for the slower fading rate are not established. A reasonable hypothesis is that ozone is partially used in attacking available hydroxyl groups. The same reason could explain the effect of surface saponification of cellulose triacetate in giving a layer of cellulose which acts as an inhibitor against ozone fading.

The action of water as a solvent for ozone provides an additional effect to that of the water as a swelling agent. Ozone has significant solubility in water and its increased absorption by the fiber would also introduce an additional absorbing medium for the reactive gas.

Ozone fading of nylon dyeings using Disperse Blue 3 and Disperse Blue 7 were studied for three different concentrations exposed to four spaced time intervals. The fading reaction was found to obey a first order law with respect to the dyestuff which implies that each

dye molecule is equally accessible to ozone in the nylon 6 fiber used. The rate constants as a measure for the fading tendency were calculated and compared for the two dyes. Disperse Blue 3 on nylon 6 exhibits a much higher fading tendency than Disperse Blue 7, whereas on cellulose triacetate the fading rates are essentially the same. The reason for this difference was looked for in the mode of attachment of the dye to the fiber. Wet bleeding tests according to AATCC Test 107-1968 showed a much higher staining tendency on the multifiber test fabric for Disperse Blue 3 on nylon 6 (step 2 on Staining Scale) than for Disperse Blue 7 (step 4 on Staining Scale).

Disperse Blue 7 compared with Disperse Blue 3 has two additional hydroxyl groups with hydrogen bonding abilities and exhibits a symmetry of substitution which can account for its much stronger attachment. A reasonable explanation for the greater resistance of Disperse Blue 7 lies in the lower rate of desorption into the water within the fiber. Since ozone fading of nylon takes place at high humidity and since ozone and disperse dye are soluble in water, the reaction may take place in the medium of the absorbed water as well as within the fiber itself.

A good argument in favor of this line of thinking is given with the behavior of blue acid dyes based on anthraquinone. Dyeings made with these dyes are resistant to ozone. Their ionic bond to the fiber molecule in addition to other forces provide a stronger attachment to the fiber and much less availability for a reaction with ozone in the water medium.

For cellulose triacetate, however, in case of ring dyeings it was

found that no humidity is necessary for the occurrence of fading, and a heterogeneous reaction seems to take place. In ring dyeings the dye is absorbed in fiber regions which are easily accessible for the dye and even easier for the smaller ozone molecules. For well penetrated triacetate dyeings, a strong dependence of rate of fading on humidity was noted.

It was concluded from the results obtained that the hypotheses set up in the beginning were supported:

- 1) The difference in incidence of fading and fading rate are dependent on the absorptivity and penetration of the causative agent ozone.
- 2) The absorptivity of the fiber for ozone will vary with the crystallinity or molecule packing of the fiber; therefore accessibility will increase when fibers are in a swollen state due to effect of absorbed water.
- 3) The destruction of dyes is due to the vulnerability of dye structures to oxidation whereby the chromophore is destroyed.
- 4) The resistance of dyes is due to the mode of attachment and the physical state of the dye within the fiber as shown in the high resistance of Disperse Blue 7 on nylon as compared to Disperse Blue 3.

Recommendations for Further Work

- 1) Disperse Blue 3 analogs of higher molecular weight and therefore better washfastness should be examined in order to assess the theory that ozone fading rate on nylon is related to

wetfastness rather than intrinsic resistance to oxidation of the dyestuff.

- 2) The effect of ozone upon nylon fiber itself should be examined in order to determine whether the nylon fiber itself consumes ozone and thereby acts as an inhibitor thus proving that fading of dyes occurs in the absorbed water rather than on the fiber polymer structure itself.

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